COMMERCIAL ORGANIC ANALYSIS

VOLUME III—PART I

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COMMERCIAL

ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION,
AND MODES OF ASSAYING THE VARIOUS ORGANIC
CHEMICALS AND PRODUCTS EMPLOYED IN THE
ARTS, MANUFACTURES, MEDICINE, &C.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

BY

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PUBLIC ANALYST FOR THE WEST RIDING OF YORKSHIRE, THE CITY OF SHEFFIELD, &C.

Third Edition, Rewritten and Enlarged

VOLUME III—PART I

TANNINS, DYES AND COLORING MATTERS, WRITING INKS

REVISED AND EDITED BY

J. MERRITT MATTHEWS, PH.D.

PROFESSOR OF CHEMISTRY AND DYEING IN THE PHILADELPHIA TEXTILE SCHOOL

REVISER'S PREFACE TO THIRD EDITION.

THE volume now issued exhibits considerable difference from the preceding edition, the first part of which was occupied with a description of the AROMATIC ACIDS. This subject has been transferred to another volume, leaving the present one to deal solely with the TANNINS, COLORING MATTERS and WRITING INKS. Both of these sections have been elaborated to a considerable extent, necessitating the rewriting of a great deal of the old material and the extensive addition of new matter.

The chapter on Tannins has been amplified with descriptions of new tannin materials and several new methods of analysis. It is to be regretted, however, that our knowledge of tannin-analysis is still in such an unsatisfactory condition, that scarcely any two methods give results which are concordant.

The chapter on Dyes and Coloring Matters has been greatly changed in its arrangement, and has been almost doubled in the amount of matter presented. The classification adopted in the former edition was found to be inadequate to the requirements of a branch of Applied Chemistry which has been remarkably productive during the past decade, and has been modified accordingly. Wherever possible, reactions have been tabulated for the purpose of avoiding needless repetition and verbiage, a method which also facilitates reference for analytical purposes.

It has been impracticable to submit either the manuscript or proof-sheets to Mr. Allen, but his co-operation has been secured in other respects, and the reviser is indebted to him for a large number of notes, references, and clippings, which have been duly utilized.

PHILADELPHIA TEXTILE SCHOOL,
        September, 1900.

CONTENTS.

TANNINS OR TANNIC ACIDS.

DYES AND COLORING MATTERS.

TANNINS.

Under the name of Tannin or Tannic Acid are known, and to a great extent confused, a considerable number of vegetable acids having great analogy to each other, but possessing distinct individuality. The different varieties of tannin or tannic acid agree in the following general properties:—

Description and General Properties of Tannins.

Tannic Acids are compounds of carbon, hydrogen and oxygen containing a benzene nucleus. They are amorphous or sub-crystalline solids of astringent taste, not fusible or volatile, more or less soluble in water, and freely so in alcohol, or a mixture of alcohol and ether, and notably in ethyl acetate. They are nearly insoluble in dry ether, and quite so in chloroform, benzene, petroleum spirit, and carbon disulphide. The tannins are generally but little soluble in dilute sulphuric acid. Their aqueous solutions give blue-black or green colorations or precipitates with ferric salts, and are all precipitated by the acetates of lead and copper and by stannous chloride. Some tannins are precipitated by tartar-emetic and by mineral acids. In some cases tannin combines with the base only, but in others, as when cupric acetate is employed, the salt enters into combination as a whole. With a solution of gelatin, the tannic acids give precipitates analogous to l e a t h e r, quite insoluble in presence of excess of tannic acid, but not wholly insoluble in pure water. Tannic acids, or most of them, can be completely removed from their aqueous solutions by the introduction of skin or rasped hide. The tannic acids are also removed from solution by digestion with cupric or zinc oxide, and they reduce Fehling's solution on heating. A delicate reaction for tannins (first noticed by the author and apparently general) is the deep red color produced on treating a solution with potassium ferricyanide mixed with ammonia. Tannic acids give insoluble precipitates with many organic bases, the rosaniline and cinchonine

2 (17)

precipitates being among the least soluble; but it is frequently observable that an alkaloid and a tannin which occur together in the same plant do not combine together to form an insoluble compound.

The most characteristic property of the tannins is the formation, by combinations with gelatin and gelatin-forming tissues, of the insoluble compounds which constitute l e a t h e r.

All natural tannins are powerful reducing agents, and exhibit a marked tendency to absorb oxygen, especially in alkaline solution. The oxidation-products are often strongly colored.

Extraction of Tannins.

The different natural tannins exhibit such differences, in their chemical reactions and behavior with solvents, that it is not possible to give a general rule for their extraction in a state of purity. The following notes indicate the nature of the methods to be pursued:—

The method of P e l o u z e for the preparation of gallotannic acid from gall-nuts is as follows:—The powdered substance is exhausted with ordinary ether containing alcohol and water. On standing, the liquid separates into two layers, the lower of which contains tolerably pure gallotannic acid, while the upper ethereal layer retains the gallic acid. The tannin obtained by separating and evaporating the lower layer may be further purified by dissolving it in water and adding to the solution twice its measure of ether, when three layers are formed, the lowest of which contains nearly pure gallotannic acid. This solution is drawn off, and crystals of magnesium sulphate are added to remove the excess of water. The ethereal solution is then evaporated to dryness.

A more generally applicable process of extracting tannins is the following:—The finely divided substance is exhausted by treatment with rectified spirit, the solution filtered, and evaporated to a small bulk at as low a temperature as possible (preferably under diminished pressure). The extract is treated at once with a considerable proportion of cold water, the liquid filtered and fractionally precipitated with acetate of lead. The first and last fractions should be rejected, as they are usually contaminated with coloring matters and other foreign substances. The tannate of lead is washed as rapidly as possible, suspended in water, and decomposed by sulphuretted hydrogen. The filtrate is shaken with ether to remove gallic acid, separated from the ethereal layer, and

evaporated in a partial vacuum to the consistence of a thin syrup. The remaining water should be removed by exposure over sulphuric acid at the ordinary temperature.

Schroeder and Bartel have investigated the effect of prolonged boiling in the extraction of tannins. They conclude that if a sufficient quantity of water is used only a few hours of boiling are necessary to extract the largest part of the tannin, succeeding extractions only drawing traces of tannin from the residue. Prolonged boiling causes more non-tannins to be dissolved, therefore it is not advisable to push the extraction too far, as the quality of the whole product will be deteriorated by the non-tannin constituents.

Parker (J. S. C. I. 1898, 106) shows that by extracting a material for a long time at a low temperature, and afterwards the same material at a higher temperature, it may be possible to isolate the different tannic acids. It was also noticed that boiling the material not only causes a loss of tannin, but also darkens the color very much. Between 60° and 90° C. seem to be the best temperatures for the extraction of tannins.

Many tannins (e. g., sumac-tannin and ratanhia-tannin) may be purified by agitating with ether to remove gallic acid, saturating the concentrated aqueous solution with common salt, and agitating it with acetic ether, which removes the tannin.

Some tannins (e. g., hop- and alder-tannin) are stated to be insoluble in water after isolation, the change being probably due to partial decomposition. When the presence of such tannins is anticipated, the lead precipitate should be suspended in alcohol instead of water, before decomposing it with sulphuretted hydrogen.

Many other vegetable bodies besides tannins are precipitable by lead acetate, but they are commonly insoluble in cold water.

It not infrequently happens that a single plant contains two or more tannins. Thus both oak- and willow-bark contain a little gallotannic acid in addition to their own peculiar tannins; and myrabolams and divi-divi contain both gallotannic and ellagitannic acids. The existence of several tannins may be detected in some cases by fractional precipitation with lead acetate, and in others by examining the products of the action of dilute acid. Thus, oak-red produced from quercitannic acid is not removed by agitating the liquid with ether, while the gallic acid produced from the co-existent gallotannic acid is dissolved by the same menstruum.

From the estimation of the amount of tannin in leaves under various conditions of light and shade, it has been shown (G. K r a u s , Jour. Franklin Inst., 1889) that light and carbon dioxide are essential agents in the production of tannin in the plant. Leaves which are not green are not capable of producing tannin. The tannin made in the leaves passes into the branches and roots, and there is no evidence to show that it undergoes any further change.   It is not yet known whether tannin is produced from non-nitrogenous substances, or whether it is formed in the conversion of nitrogenous compounds into albuminoids.

Constitution of Natural Tannins.

From the tanner's point of view, the natural tannins may be arranged in two great classes, namely, those which produce a "bloom," or fawn-coloured deposit, on leather, and those which do not.   The tannins giving a bloom to leather give a blue-black coloration with ferric acetate, while the others afford a green colour with the same reagent.   To the first of these classes belong the tannins of gall-nuts, myrabolams, divi-divi, sumach, valonia, and oak-bark, while the second includes the tannins of catechu, hemlock, larch, ratanhia, mangrove, and all the varieties of mimôsa. The production of the "bloom" is in most cases due to the formation of e l l a g i c   a c i d, $C_{14}H_8O_9$, a body allied to g a l l i c a c i d, $C_7H_6O_5$, of which most of the tannins of the first group may be considered to be derivatives.   The tannins of oak-bark and valonia are either mixtures of two distinct tannins or of anomalous character, for they yield both gallic acid and protocatechuic acid, $C_7H_6O_4$; while all the tannins which give a green reaction with ferric acetate are derivatives of the latter of these acids. These again may be divided into tannins which yield a c e t i c or some other f a t t y   a c i d on fusion with potash, and those which yield p h l o r o g l u c o l, $C_6H_6O_3$.

It has been shown by H. S c h i f f [1] that the ordinary tannin of galls (gallotannic acid) is in great part a glucoside, and that under the influence of dilute acids, or of a peculiar nitrogenous ferment called p e c t a s e, it splits up into glucose and gallic acid, thus:—

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[1] Owing to the optical activity of commercial tannin, Schiff suggested a formula by which the substance is represented as containing an asymmetric carbon atom. W a l d e n' s experiments (Ber. xxx. 3151), however, show that commercial tannin is not only a mixture, but also varies in composition, and, therefore, its optical behavior cannot be used in a theory regarding its structure.

$C_{34}H_{28}O_{22} + 4H_2O = C_6H_{12}O_6 + 4C_7H_6O_5$. Many other of the natural tannins also furnish glucose by the action of dilute acids, but in some cases the change occurs with much less facility than is usual with glucosides. Hence it has been suggested by H l a s i e-w e t z that the tannins are not true glucosides, but bodies which would be more correctly regarded as gummides or dextrides,[1] and hence that the formation of glucose by the action of dilute acids is due merely to a secondary action on the gum or dextrin. Some of the natural tannins certainly yield no glucose by the action of dilute acid, and in other cases its formation is still an open question.

The arrangement of natural tannins into classes is therefore based on the products they yield:—(1) when heated alone, (2) when heated with dilute acid, and (3) when fused with caustic alkali. The characteristic products obtained by heating tannins alone are p y r o g a l l o l and c a t e c h o l; by heating with dilute acids, g l u c o s e, g a l l i c a c i d, e l l a g i c a c i d, and insoluble amorphous anhydrides called p h l o b a p h e n e s; and by fusion with caustic alkali, p y r o g a l l o l, p r o t o c a t e c h u i c a c i d, a c e t i c a c i d, and p h l o r o g l u c o l.

In the table on page 23 the principal kinds of tannin are arranged according to the foregoing principles of classification.

Certain of the tannins give a blue or black coloration when mixed in solution with ferric salts, while others yield a green or greenish color when similarly treated. Speaking generally, the tannins which are derived from gallic acid give a blue reaction, while those derived from protocatechuic acid afford a green color.

The reaction with iron salts is best observed by adding to an aqueous solution of the tannin contained in a test-tube one or two drops of a dilute solution of ferric acetate. This may be extemporized by adding sodium acetate to a solution of ferric chloride. Excess of the reagent must be avoided, or its color and oxidizing action may lead to error. The coloration produced by ferric acetate having been observed, it is advisable to add an excess of ammonia, and note any change which may occur.

If ferric chloride be substituted for the acetate, the general results are the same, but in some instances a greenish coloration is produced by tannins which give a distinct blue reaction with ferric acetate, and are undoubted gallic acid derivatives. This is

[1] Valonia is liable to a natural fermentation (ropiness), in which large quantities of dextrin, or some similar body precipitable by alcohol, are formed.

especially the case if the ferric chloride solution contains free acid. Hence the acetate is much to be preferred as a reagent for tannins. Other reactions of tannins are given on pages 24 and 25.

Prescott[1] gives the following comparative table of the different kinds of tannins:

(1) Glucoside-tannins. When boiled with dilute mineral acids yield (*a*) a crystallizable acid, or its anhydride, or (*b*) a phlobaphene and a glucose.

(2) Iron-bluing tannins with ferric salts give blue to black precipitates or colors. The ferroso-ferric solutions, slightly basic, give the best reactions. Mineral acids dissolve and decolor.

(3) Tannins not tanning agents. Do not form leather, nor preserve animal membrane, though precipitating solutions of gelatin.

(4) Tannins which in subliming, or in fusing with potassium hydroxide, yield a trihydroxyphenol, such as Pyrogallol, $C_6H_3(OH)_3$.

(5) Pathological tannins. Found in punctured vegetable tissue. Gallo-tannins, including sumac-tannin.

(1) Tannins not glucosides.

(2) Iron-greening tannins,[2] with basic ferric salts, give greenish precipitates or colors. Brown colors sometimes obtained.

(3) Tanning materials. Change animal membrane into leather, not putrescible. Also precipitate solutions of gelatin.

(4) Tannins which in subliming, yield a dihydroxyphenol, $C_6H_4(OH)_2$, and on fusion with potash, yield an acid as protocatechuic acid, $C_6H_3(OH)_2CO_2H$.

(5) Physiological tannins. From uninjured vegetable tissues. Include various glucosides and iron-bluing tannins.

Distinction between Alcoholic and Aqueous Tannins.—This distinction is of considerable importance, as in some countries a duty is only collected on alcoholic tannin. A tannin which has been prepared by extraction with water, on treatment with ether and a subsequent evaporation of the ethereal extract, leaves a residue which redissolved in alcohol, does not precipitate on the addition of water. On the contrary, a tannin which has been prepared by extraction with alcohol, gives under the same conditions a distinct precipitate, due to the fats and resins which accompany it.

The following is a description of the best methods of operating with a view to the formation and recognition of the decomposition-products obtained by the action of heat, dilute acids, and fusing potash on the different kinds of tannin.

[1] Organic Analysis, 1895.

[2] Of this class only willow-tannin is a glucoside.

Tannin.	Source.	Formula.	Products on heating with Dilute Acid.	Products of dry Distillation.	Products on Fusion with Caustic Potash.	Reaction with Ferric Acetate.	Remarks.
Digallic acid, · · ·	Gall-nuts.	$C_{14}H_{10}O_9$.	Gallic acid only.	Pyrogallol.	Pyrogallol and carbonic acid.	Blue-black.	
Gallotannic acid (Glucoside), · · ·	Gall-nuts.	$C_{34}H_{28}O_{22}$.	Gallic acid and glucose.	Pyrogallic and metagallic acids.	Pyrogallol and carbonic and glucic acids.	Blue-black.	
Ellagitannic acid, · ·	Divi-divi; myrabolans.	$C_{14}H_{10}O_{10}$.	Ellagic acid only.	Pyrogallol.	· · ·	Nearly black.	
Sumac-tannin, · · · ·	Sumac leaves.	$C_{19}H_{14}O_{10}$.	Gallic acid.	Do.	· · ·	Blue-black.	Possibly identical with gallotannic acid.
Pomegranate-tannin.	Pomegranate rind.	· · ·	Ellagic acid and glucose.	Do.	· · ·	Blue-black.	
Caffetannic acid, · ·	Coffee berries.	$C_{14}H_{16}O_7$.	Caffeic acid and glucose.	Catechol.	Protocatechuic and acetic acids.	Green.	
Cinchotannic acid, · ·	Cinchona-bark.	$C_{14}H_{16}O_9$.	China red and glucose.	Do.	Do. do.	Green.	Very soluble in ether, &c.; two varieties exist.
Fern-tannin, · · · · ·	Male-fern.	· · ·	Fflix-red and glucose.	Do.	Do. do.		
Maté-tannin, · · · Valonia-tannin, · · ·	Paraguay tea. Valonia.	· · ·	?and glucose. Valonia red.				
Quercitannic acid, · ·	Oak-bark; tea-leaves.	$C_{19}H_{16}O_{10}$.?	Oak red.	Catechol and Pyrogallol.	Protocatechuic and gallic acids.	Blue-black.	
Ulmotannic acid, · ·	Elm-bark.	· · ·	Elm red.	Do.	Protocatechuic acid and phloroglucol. Do.	Blue-black.	Probably identical with oak tannin.
Salitannic acid, · · · ·	Willow-bark.	$C_{17}H_{17}O_9$.	Phlobaphene.	Catechol.	Do.	Deep black.	
Lingue-tannin, · · · ·	Laurus caustica.	$C_{20}H_{18}O_{10}$.	Phlobaphene.	Do.	Do.	Green.	
Hemlock-tannin, · · ·	Hemlock.	$C_{38}H_{34}O_{18}$.	Hemlock red.	Do.	Do.	Green.	
Catechu-tannic acid, · ·	Catechu.	$C_{28}H_{21}O_{11}$.	Catechin.	Do.	Do.	Greenish.	
Kinotannic acid, · · ·	Kino.	· · ·	Kino red.	Catechol and phenol.	Do.	Green.	Alcoholic solution gelatinizes.
Ratanhia-tannin, · · ·	Ratanhia.	· · ·	Ratanhia red.	· · ·	Do.	Green.	Does not precipitate tartar-emetic.
Chestnut-tannin, · · ·	Horse-chestnut.	$C_{36}H_{24}O_{12}$.	Chestnut red.	· · ·	Do.	Green.	Does not precipitate tartar-emetic.
Morintannic acid, · · ·	Fustic.	$C_{13}H_{10}O_6$.	Rufimoric acid.	Catechol.	Do.	Greenish.	Crystallizable: yellow.
Tormentil-tannin, · ·	Tormentilla.	· · ·	Tormentil red.	Catechol.	Do.	Green.	
Quebrachitannic acid	Quebracho lorentzii.	· · ·	Quebracho red.	· · ·	Do.	Green.	Precipitates gelatin and albumin.
Alder-tannin, · · · · ·	Alder-bark.	$C_{27}H_{28}O_{11}$.	Alder red and glucose.	Do.	Phloroglucol and protocatechuic and acetic acids. Do.	Dirty green.	Insoluble in water after extraction. Does not ppte. tartar-emetic.
Lupulo-tannic acid, ·	Hops.	$C_{25}H_{24}O_{13}$.	Hop red and glucose.	Do.	Do.	Greenish.	
Animal tannin, · · · ·	Corn weevils.	$C_{28}H_{16}O_{16}$.	· · ·	· · ·	· · ·	Blue-black.	

Reaction of Tannins: Action of Heat.

When a tannin which produces a "bloom" on leather (Class A) is cautiously heated to about 200° C., it is decomposed with volatilization of p y r o g a l l o l in feathery crystals. On the other hand, the tannins which produce no bloom, but red deposits, give a somewhat similar reaction, but the sublimate consists of c a t e - c h o l. From oak-bark and valonia, which apparently contain a mixture of both kinds of tannin, and hence yield both bloom and red coloring matters, both catechol and pyrogallol are produced on heating.

In using the heating test for distinguishing the two classes of tannins, the temperature must be carefully regulated, or much loss will ensue and the recognition of the pyrogallol or catechol will be greatly complicated by the formation of metagallic acid and other secondary products. A better result is obtained by mixing the substance with several times its weight of sand or powdered pumice, and passing a stream of coal-gas or carbon dioxide through the retort, so as to carry the products quickly out of the heated space. A still better and more convenient plan is the following, based on an observation of T. E. T h o r p e (*Chem. News*, xliii. 109):— About 1 gramme of the sample should be heated with 3 c.c. of pure glycerin to a temperature of 190° to 200° C. for twenty minutes. After cooling, the product is treated with about 20 c.c. of water, and the liquid shaken with an equal measure of ether without previous filtration. The ethereal layer, which contains the pyrogallol and catechol, is separated from the aqueous liquid, evaporated to dryness, and the residue dissolved in 50 c.c. of warm water. The filtered solution is divided into several portions which are respectively tested with lime-water, ferric chloride, and ferric acetate. These reagents readily distinguish catechol from pyrogallol when unmixed, and will suffice for the recognition of the one in presence of not too large a proportion of the other. It must be remembered that the production of pyrogallol may have resulted from the presence of gallic acid in the original substance, if the tannin had not previously been purified therefrom in the manner indicated on page 18. Catechol, on the other hand, may be a product of the decomposition of catechin and other bodies allied to and associated with tannins, unless care has been taken to remove them previously. As a general rule, however, catechins and catechol-derivatives only occur in quantity with catechol-tannins, and the same is true of gallic acid with regard to pyrogallol.

The characters of pyrogallol and catechol have already been fully described (Vol. II., pt. II.)

Action of Dilute Acids on Tannins. Phlobaphenes.

As already stated, many tannins are resolved on heating with dilute acids into g l u c o s e, and either gallic acid, ellagic acid, or an amorphous, insoluble, red coloring matter or p h l o b a p h e n e, according to the nature of the tannin. Other tannins yield these products without glucose being simultaneously formed. As a rule, the action of dilute acid on a tannin results in the formation, apart from glucose, of a single decomposition-product belonging to the aromatic series (*e. g.*, gallic acid, ellagic acid, phlobaphene, &c.), but in some cases two or more of such bodies are producible from a tannin of apparently homogeneous nature (page 19).

To ascertain whether a tannin yields glucose by hydrolysis, it should first be carefully freed from any admixture of ready-formed carbohydrates by precipitation with neutral lead acetate, or saturation of the aqueous solution with salt and removal of the tannin by agitation with acetic ether, in the manner indicated on page 18. The washed lead salt, or the tannin left on evaporating the acetic ether, is then heated to 100° C. for some hours, with dilute hydrochloric acid, in a sealed tube or firmly closed bottle. (Mere boiling with the dilute acid, replacing loss by evaporation, is sufficient in most cases, especially for qualitative purposes.) After cooling and opening the bottle, the mixture should be allowed to stand for some time in the cold, to observe whether any sparingly-soluble decomposition-product separates.[1] In such case, the precipitate should be filtered off, and any traces remaining in solution removed by agitating the filtrate first with acetic ether and then with ordinary ether. The aqueous liquid is boiled, neutralized with soda, precipitated with basic lead acetate (to remove any traces of tannin or coloring matters), the liquid again filtered, the excess of lead removed by dilute sulphuric acid, the filtered liquid again neutralized by soda, and heated to boiling with Fehling's solution, when a yellow or red precipitate of cuprous oxide will prove the presence of glucose. This latter may also be shown by a fermentation test with yeast, or by an optical examination as to rotatory power.

[1] To prevent subsequent source of error, it is desirable to get rid of any ready-formed gallic acid, by repeatedly agitating the solution of the tannin with ether before precipitating with lead acetate.

The *precipitate* produced on cooling the product of the action of dilute acid on the tannin may consist of lead chloride (if the lead compound has been used), ellagic acid, or a phlobaphene. The lead chloride may be removed by washing with boiling water. If the residue has a pale yellow or fawn color, and is but slightly soluble in cold alcohol, it probably consists of e l l a g i c   a c i d, which is soluble in ammonia and hot alcohol, and dissolves readily in strong nitric acid with intense crimson coloration. A red residue, readily soluble in cold alcohol, will consist of a p h l o b a - p h e n e, which will be reprecipitated on diluting the alcoholic solution with water, and may be further examined by fusion with caustic potash.

The *ethereal layer*, obtained by shaking the filtrate from the ellagic acid and phlobaphenes with ether and acetic ether, will contain g a l l i c   a c i d, if any has been produced by the treatment of the tannin with dilute acid. For its recognition the ethereal solution should be evaporated to dryness, the residue taken up with cold water, and the solution filtered. The filtrate will give a fine red coloration with potassium cyanide, if gallic acid has been produced. The reaction may be confirmed by treating another portion of the filtrate with an aqueous solution of picric acid, followed by ammonia, when a reddish coloration, changing to a fine green, will be produced if gallic acid be present.

In many cases it is not necessary to employ so elaborate a process as the foregoing in order to distinguish the class to which a tannin belongs, It is frequently sufficient to boil the tannin or its infusion with dilute hydrochloric acid for some time, replacing the acid lost by evaporation. The solution is then diluted and allowed to cool, when ellagic acid and phlobaphenes will separate, and may be filtered off and separated by treatment with cold alcohol as already indicated.

G a l l i c   a c i d as well as E l l a g i c   a c i d have been fully described in Vol. II., pt. II.

PHLOBAPHENES.

Chemically, the phlobaphenes are a n h y d r i d e s of the respective tannic acids from which they are derived, or, in other words, they are formed from these tannins by the loss of one or more molecules of water. In this way they are produced by the action of dilute acids on tannins, and may also be formed in many cases by pouring alcoholic or highly concentrated aqueous solutions of the tannins into cold water, under which circumstances a part of

the tannin seems unable to assimilate water and the phlobaphene separates as a red precipitate. Phlobaphenes exist ready-formed in most tannin materials capable of producing them, and may be dissolved out of these or the dried extracts thereof by means of alcohol.

The phlobaphenes are red or brown amorphous bodies, difficultly soluble in pure or acidulated water or in pure ether, but soluble in water containing ammonia, and freely soluble in spirit. Some phlobaphenes are so sparingly soluble in water, even when boiling, that the character may be utilized for the determination of the corresponding tannin. This is especially the case if, after heating with hydrochloric acid, the liquid be evaporated to dryness and the residue treated with water. The decomposition-products then often remain almost entirely undissolved, but not wholly so, for, though mostly insoluble in pure water, they are dissolved more or less by solutions of sugar and other substances. The phlobaphenes are also dissolved by dilute alkalies and alkaline carbonates, and by borax, which last substance is said to be used in the preparation of some tannin extracts, and has been suggested as a means of rendering phlobaphenes available for tanning. The solubility of the phlobaphenes in water depends much on their degree of hydration, many tannins giving a whole series of anhydrides, of which those containing only one molecule of water less than the original tannin are quite soluble in water, while the higher members of the series become less and less soluble as they lose water. The soluble phlobaphenes are the coloring matters of tanning materials, and behave like the tannins themselves, precipitating gelatin and combining with hide to form leather.[1]

In many cases (e. g., gambier) it is certain, and in others it is probable, that the tannin itself is merely the first anhydride of the series, and is derived from a catechin which is itself white, crystallizable, and destitute of tanning properties.

The phlobaphenes somewhat resemble the resins in their analytical characters, as, for instance, their solubility in alcohol and slight solubility in water, and in their behavior when fused with

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[1] Hemlock-bark yields a series of such bodies, of which the lower members are deep-red soluble tannins, and the higher form the red sediment which occurs in hemlock extract. It is not possible to decolorize hemlock extract without at the same time greatly reducing its tanning powers, though by preparing and concentrating it at a low temperature the proportion of insoluble higher anhydrides formed may be kept at a minimum.

caustic alkali; but they are distinguished from the resins by dissolving in dilute ammonia.   With gelatin, ferric acetate, and lead acetate the phlobaphenes usually react like their respective tannic acids.   Occasionally a so-called tannin is met with (*e. g.*, hoptannin), which is not precipitated by gelatin, while the phlobaphene therefrom is precipitated.

Phlobaphenes are yielded by the tannic acids from the bark of the oak, elm, horse-chestnut, willow, birch, fir, and acacia, as well as by the tannins from rhubarb, male-fern, wine, &c.   According to G r a b o w s k i, the phlobaphenes from the tannins of the oak, ratanhia, and tormentilla are not merely analogous to but actually identical with chestnut-red (see Quercitannic Acid, Vol. II., part II.).

Action of Fused Alkali on Tannins.   Phloroglucol.

When tannins are subjected to the action of caustic alkali in a state of incipient fusion, they are broken up with formation of products varying with their constitution.   Thus all the tannins yielding catechol on dry distillation, that is, all those which give a green colour with ferric acetate—and valonia and oak-bark tannins in addition—give p r o t o c a t e c h u i c   a c i d when fused with caustic potash.   On the other hand, those tannins which give pyrogallol when heated alone yield gallic or ellagic acid when fused with caustic alkali.[1]   In each case the reaction consists in the elimination of CO_2.

The tannins which yield protocatechuic acid on fusion with alkali may be further subdivided according to the secondary product formed simultaneously, one class giving acetic or some other fatty acids, and a second a body called p h l o r o g l u c o l (page 30).[2]   A third class, including the tannins of the alder and hop,

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[1] The relationship of these products of the decomposition of tannins is shown by the following formulæ:

Protocatechuic acid
(Dihydroxybenzoic acid) C_6H_2 $\begin{cases} OH^{(1)} \\ OH^{(2)} \\ H \\ CO.OH^{(4)} \end{cases}$ $- CO_2 =$ Catechol
(Pyrocatechin) C_6H_2 $\begin{cases} OH^{(1)} \\ OH^{(2)} \\ H \\ H \end{cases}$

Gallic acid
(Trihydroxybenzoic acid) C_6H_2 $\begin{cases} OH \\ OH \\ OH \\ CO.OH \end{cases}$ $- CO_2 =$ Pyrogallol
(Pyrogallic acid) C_6H_2 $\begin{cases} OH^{(1)} \\ OH^{(2)} \\ OH^{(3)} \\ H \end{cases}$
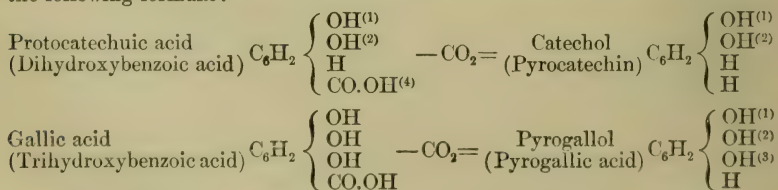
[2] The formation of these products is due to a reaction allied to saponification, thus:

$$C_{13}H_{10}O_6 + KHO = KC_7H_5O_4 + C_6H_6O_3.$$

Morintannic   Potassium   Phloro-
Acid.   Protocatechuate. glucol.
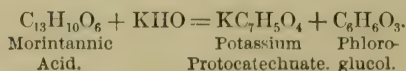
give both acetic acid and phloroglucol, but this peculiarity is not improbably due to the coexistence of two distinct tannins.[1] All those tannins which yield acetic acid instead of phloroglucol on fusion with potash give notable proportions of glucose on heating with dilute acid, while some, and probably all, of the phloroglucol-tannins give no sensible quantity of glucose.

To recognize the presence of a phloroglucol-tannin without employing the tedious method described below, H. R. Procter mixes 5 c.c. of water, 1 c.c. of a saturated solution of commercial nitrate of aniline, and 1 c.c. of a very dilute solution of potassium nitrite. To this liquid is added 1 c.c. of a solution containing as nearly as possible $\frac{1}{2}$ per cent. of the tannin to be examined. If phloroglucin or phloroglucide-tannin be present the liquid will gradually become yellow or orange, and will deposit a cinnabar-red precipitate after standing for a time not exceeding one hour, but many other bodies give precipitates which may lead to mistaken conclusions. Thus the reaction is produced by oak-bark infusion, which is not supposed to contain a phloroglucol-tannin, and gall-tannin, pyrogallol, and other substances give similar but browner precipitates. A sharper distinction may be obtained by employing more dilute solutions, but it is preferable, when possible, to act on the tannin with fusing potash and examine the products.

The fusion with potash may be conducted either on the original tannin or on the body produced by treating it with dilute acid. When convenient, the lead salt may be substituted for the free tannic acid. The separation or recognition of protocatechuic and gallic or pyrogallic acids when mixed is very troublesome, and hence it appears better in most cases simply to aim at the isolation and recognition of phloroglucol. The following is the method usually prescribed for this purpose:—20 grammes of the tannin, phlobaphene, or lead salt are boiled with 150 c.c. of solution of caustic potash, of 1.2 specific gravity, for two or three hours, and the liquid then concentrated with continual stirring till it becomes pasty, the alkali undergoing fusion.[2] The product is cooled, and treated with dilute sulphuric acid in quantity sufficient to render the whole distinctly acid when cold, the liquid is filtered from the

[1] The fusion of gallic acid with caustic soda is said to result in the formation of a small quantity of phloroglucol (*Jour. Chem. Soc.*, xliv. 60).

[2] In some cases, such as that of phloretin, it is sufficient to boil the substance with caustic potash solution, as described in the text, omitting the subsequent evaporation and fusion.

potassium sulphate and other solid matters, and the filtrate is treated with sodium bicarbonate till its wine-red reaction with litmus (or absence of red coloration with methyl-orange) shows that the sulphuric acid is neutralized. The liquid is then shaken several times with ether, and the ethereal solution evaporated. The residue contains phloroglucol, recognizable by its sweet taste and reactions with ferric chloride and fir-wood. If necessary, it may be purified from protocatechuic acid by precipitating the aqueous solution with neutral lead acetate, the filtrate being extracted with ether, or evaporated after separating the excess of lead by sulphuretted hydrogen.

PHLOROGLUCOL. PHLOROGLUCIN. $C_6H_6O_3$. This substance is isomeric with pyrogallol and hydroxyquinol, and is generally regarded as s y m m e t r i c a l t r i h y d r o x y b e n z e n e, but there is evidence in favor of a different constitution.[1] It is possible that it exists in both forms, one of which is readily converted into the other. Phloroglucol forms small plates or rhombic tablets containing $2H_2O$. It becomes anhydrous at 100°, and melts at 218° if heated rapidly, but at 209° or even 200° if slowly heated. At a higher temperature it sublimes without odor, and solidifies again on cooling.

Phloroglucol is sweeter than cane-sugar. It is soluble in water and alcohol, and readily in ether, and by agitation with the last solvent can be removed from its aqueous solution. An aqueous solution of phloroglucin is not precipitated by any metallic salt except basic lead acetate. It is colored deep violet by ferric chloride, and reduces Fehling's solution and ammonio-nitrate of silver. In concentrated aqueous solution it is converted by bromine into t r i b r o m o - p h l o r o g l u c o l, $C_6H_3Br_3O_3$, which immediately separates in long needles, the liquid emitting a powerful, tear-exciting odor.

When dilute solutions of phloroglucol and nitrate of toluidine or aniline are mixed, and a very dilute solution of potassium nitrite added, the liquid gradually becomes turbid and of a brown-
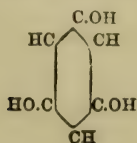
[1] Symmetrical Trihydroxybenzene.   Modified Formula of Phloroglucol.
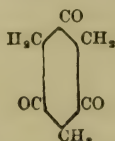
ish-yellow color, then orange-red, and finally a vermilion-red precipitate is produced. The reaction is extremely delicate.

If a freshly-cut slip of deal be moistened with a dilute solution of phloroglucol ($\frac{1}{2}$ per cent.), and subsequently with dilute hydrochloric acid, it acquires an intense violet or red colour. The reaction is very delicate.[1]

Action of Other Chemicals.

By heating a mixture of tannin, potassium bisulphate and acetacetic ether to 190°–200°, two different compounds are obtained: 1. D i t a n n a c e t a c e t i c e t h e r, $C_{34}H_{32}O_{22}$, a yellowish-grey powder, slightly soluble in cold water and decomposed by hot water; soluble in alcohol and acetic ether. 2. T a n n a c e t a c e t i c e t h e r, $C_{20}H_{20}O_{12}$, scarcely soluble in either cold or hot water, readily soluble in alcohol, ether and acetacetic ether. By the action of glycerin on a mixture of tannin and potassium bisulphate bodies are produced which, according to their empirical formula, are reduced anhydro derivatives of tannin or gallic acid, with properties similar to hydroquercitannic and hydroquergallic acids, the reduction products of the oak-bark tannic acids. From the mixture so obtained have been isolated: 1. H y d r o t a n n i c a c i d, $C_{14}H_{14}O_{7}$, possessing the properties of tannin, but with stronger reducing power. It is a brown powder, soluble in ammonia, alcohol and dilute acetic acid, but insoluble in water. 2. I s o h y d r o t a n n i c a c i d, $C_{14}H_{14}O_{7}$. H_2O, a brown powder, soluble in ammonia and dilute boiling alcohol, and slightly so in hot water, but insoluble in cold water.

If tannin is heated with glycerin or grape sugar, a compound is formed which is readily soluble in water and dilute acetic acid, and which has the property of being again decomposed into its original parts with steam. The tannin glyceride is obtained as a colorless or slightly brownish-colored syrup, while the glucoside is a solid body which forms a syrup with water.

Alterations in Tannin Substances.

P. S i s l e y in *Revue gen. des Mat. Colorantes*, 1897, No. 7, gives a resumé of the effect of various agents on tannin substances. He finds that tannin solutions when exposed to the air absorb oxygen, and become brown in color. A series of oxidation prod-

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[1] The coloration is readily obtained with infusion of gambier and probably of other phloroglucol tannins, but is also given by catechol.

ucts is obtained which is acid in character, and renders tannin so-
lutions unfit for mordanting for light shades.   The oxidation does
not seem to be dependent upon fermentation, and takes place more
rapidly in dilute than in concentrated extracts.   The presence of
acid retards the coloration, whereas alkalies favor it in consequence
of the phenolic character of tannin.   Reducing agents bring
about a decolorization of dilute tannin solutions, which, how-
ever, is not permanent, the reducing agent itself becoming oxi-
dized, which facilitates rather than impedes the oxidation of the
tannin.   The protosalts of metals which are capable of different
degrees of oxidation and which act as oxygen carriers act similarly.
With concentrated extracts sulphurous acid is useful and preserves
them comparatively well, but with diluted extracts the sulphurous
acid is oxidized too rapidly and becomes useless.   Arsenious and
phosphorous acids, however, give very favorable results when used
in small quantities.

Dilute acids appear to hydrolyze tannins at boiling temperatures
with the formation of gallic acid.

Solutions of tannins contain usually varying quantities of nitro-
genous and pectic substances, glucosides, and mineral constituents,
and in consequence is very favorable for the growth of ferments.
This fermentation appears to convert the tannin by hydration into
gallic acid at first; further decomposition then takes place and
carbonic, butyric, oxalic, and lactic acids are formed.   The glu-
cosides present undergo alcoholic fermentation and give rise to the
wine-like odor to be noticed in fermented extracts.   After a com-
parative study of the action of various antiseptics, it is found that
boric acid is the only one which gives any good result in retarding
fermentation and preventing loss of tannin.

Gallotannic Acid.   Tannic Acid.   Tannin.

Gallotannic acid occurs in gall-nuts in proportions commonly
ranging from 60 to 77 per cent., and is usually prepared there-
from by the method of P e l o u z e described on page 18.[1]

A preferable and more modern plan is to extract gall-nuts with
a mixture of 12 parts of ether and 3 of alcohol, 12 parts of water

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[1] A further purification may be effected by fractionally precipitating the aqueous
solution of the product by acetate of lead, the first and last fractions being rejected.
The lead tannate is then treated with a quantity of solution of oxalic acid insuffi-
cient for its complete decomposition, and the liquid filtered and evaporated, first
at 100° C., and subsequently *in vacuo*.

being added to the extract, and the alcohol and ether removed by distillation.   The residual aqueous solution is then filtered and evaporated, the product being further purified by solution in water and treatment with animal charcoal.   In order to obtain the tannin in a spongy form, the syrupy solution should be mixed with some alcohol and ether and evaporated at a moderate temperature.   The spongy form is desirable as it dissolves very readily.

Pure gallotannic acid may also be obtained, according to Schiff, by extracting gall-nuts with anhydrous ether to which 5 per cent. of alcohol has been added.

As prepared by Pelouze's process, tannin yields more or less glucose or an analogous body when treated with dilute acids (the amount obtained varying from 0 to 22 per cent.), gallic acid being formed at the same time.   Hence ordinary tannin is commonly regarded as a g l u c o s i d e of g a l l i c a c i d and represented by the empirical formula $C_{34}H_{28}O_{22}$, which would yield 23 per cent. of glucose on hydrolysis.   As prepared by Schiff's process, however, gallotannic acid yields little or no glucose on treatment with dilute acid, and hence is not a glucoside, though agreeing in its other characters with the product obtained by Pelouze's method. It appears probable, therefore, that the latter contained an admixture of actual glucose, or of a glucoside brought into solution by the water present, just as oak-bark tannin is liable to contamination by lævulin or the lævulose formed therefrom.

H. S c h i f f has obtained gallotannic acid synthetically by drying gallic acid at 110°, mixing it into a thin paste with phosphorus oxychloride, and heating the mixture first to 100° and then to 120° C.   Much hydrochloric acid is evolved, and the gallic acid is converted into a yellow powder, which should be washed with ether and dissolved in water.   The unchanged gallic acid is allowed to crystallize out, after which the solution is saturated with common salt, the precipitated tannin is washed with brine and redissolved in ether alcohol.   The product thus obtained gives all the reactions of purified gall-tannin, but is perfectly reconverted into gallic acid on boiling with hydrochloric acid, without the formation of any trace of glucose or ellagic acid.   Gallotannic acid may also be prepared synthetically by oxidizing gallic acid with silver nitrate, or by boiling with dilute arsenic acid.

It may now be considered fully established that pure gallotannic acid or tannin from galls has the composition $C_{14}H_{10}O_9$, and in constitution is the first a n h y d r i d e o f g a l l i c a c i d, or d i-

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g a l l i c a c i d.[1] Its relation to gallic acid and some other allied bodies is shown by the following formulæ:—

Gallic acid. Trihydroxy-benzoic acid, $CO \begin{cases} C_6H_2(OH)_3 \\ OH. \end{cases}$

Gallotannic acid. Digallic acid, $CO \begin{cases} C_6H_2(OH)_3 \\ O.C_6H_2(OH)_2.COOH. \end{cases}$

Ellagitannic acid, . . . $CO \begin{cases} O.C_6H_2(OH)_3 \\ O.C_6H_2(OH)_2.COOH. \end{cases}$

Ellagic acid, ... $CO \begin{cases} O.C_6H_2(OH)_2{-}O \\ O.C_6H_2(OH)\diagdown COOH. \end{cases}$

Sumac-tannin, ... $CO \begin{cases} C_6H_3(OH)_3 \\ O.C_6H_2(OCH_3)_2.COOH. \end{cases}$

Kinoïn, ... $CO \begin{cases} C_6H_2(OH)_3 \\ O.C_6H_4(OCH_3). \end{cases}$

Protocatechuic acid, . . . $CO \begin{cases} C_6H_3(OH)_2 \\ OH. \end{cases}$

Quercitannic acid (?), . . $CO \begin{cases} C_6H_3(OCH_3)_2 \\ O.C_6H_2(OH)(OCH_3).COOH. \end{cases}$

The foregoing formula for gallotannic acid explains satisfactorily the following reactions:—

1. The formation of g a l l i c a c i d by hydrolysis:—$C_{14}H_{16}O_9 + H_2O = 2C_7H_6O_5$.

2. The formation of g a l l a m i d e and ammonium g a l l a t e in almost theoretical proportions by boiling gallotannic acid with aqueous ammonia in an atmosphere of hydrogen:—

$$C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.CO_2H + 2NH_3$$
$$= C_6H_2(OH)_3.CO.NH_2 + C_6H_2(OH)_3.CO_2.NH_4.$$
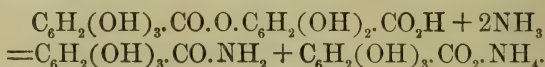
3. The formation of a p e n t - a c e t y l - d e r i v a t i v e by boiling tannin with acetic anhydride for one hour, the five hydroxyl groups being replaced by a corresponding number of C_2H_3O groups.

4. The formation of t a n n i n, or a body giving all its reactions, by heating monobromo-protocatechuic acid with potassium gallate and alcohol: — $C_6H_2(OH)_3.COOK + BrC_6H_2(OH)_2.COOH = KBr + C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.COOH.$

Pure gallotannic acid forms a colorless amorphous mass, light

[1] P. W a l d e n (*Ber.*, 1899, 3167), has shown that the molecular weight of tannin is two to four times that of digallic acid. Spectroscopic investigation of tannin and digallic acid also shows that their absorptive powers for all regions of the spectrum are entirely different, the extinction co-efficient of tannin being always considerably lower than that of digallic acid.

yellowish buff-colored scales, or brittle vitreous masses. It becomes yellow in the light even if air be excluded. The taste is strongly astringent, and the reaction acid. When heated it darkens with or without fusing, and at 215° decomposes with volatilization of water, pyrogallol, and carbon dioxide, while a residue of m e t a - g a l l i c or m e l a n o g a l l i c a c i d, $C_6H_4O_2$, is left. This last substance is the sole product when tannin is rapidly heated to 280°, and is a black, amorphous, tasteless mass.

Gallotannic acid is soluble in 6 parts of cold water, and more readily in hot. It is precipitated from its concentrated solution by dilute hydrochloric or sulphuric acid, common salt, and potassium chloride and acetate, but not by sodium sulphate or nitric acid. Skin and other gelatinous tissues remove it completely from its aqueous solution.

In absolute alcohol gallotannic acid only dissolves sparingly, but it is soluble with great facility in hydrous alcohol. In absolutely dry ether free from alcohol tannin is almost insoluble, but if water be gradually added the tannin first coagulates and then deliquesces, and after a certain portion of water has been added the liquid separates into three layers. This happens when 100 grammes of tannin are treated with 150 c.c. of ether, and 100 c.c. of water added. The lowest layer is a concentrated aqueous solution of tannin; the middle layer contains some tannin and much water; while the uppermost layer consists of ether holding a little tannic acid in solution.

Gallotannic acid is practically insoluble in chloroform, benzene, petroleum ether, and carbon disulphide. In acetic ether and in glycerin it dissolves readily.

When taken internally gallotannic acid appears to be converted into gallic acid, which may afterwards be found in the blood and urine. Tannin diffuses but slowly in aqueous solution, but may be dialyzed from its solution in alcohol.

Gallotannic acid is readily oxidizable. It reduces the salts of gold, silver, mercury, and copper, permangates, etc. Nitric acid rapidly oxidizes it, with formation of oxalic acid; and chlorine, bromine, iodine, and chromic acid act violently.

Gallotannic acid decomposes carbonates and acts as a monobasic acid. Its solution in caustic alkali rapidly oxidizes, and acquires a brown color. The g a l l o t a n n a t e s are amorphous and difficult to prepare pure. Most of them are insoluble.

One of the most important and characteristic reactions of gallo-

tannic acid is the formation of a white (or buff-colored) flocculent precipitate with a solution of gelatin. The precipitate, which is the basis of l e a t h e r, and is sometimes called t a n n a t e of g e l - a t i n, is not completely insoluble in pure water, but is wholly insoluble in presence of excess of tannic acid. When freshly formed it is often extremely finely divided, and passes through the closest filter, but becomes coagulated by adding ammonium chloride, alum, and certain other neutral salts.

Added to a dilute solution of gallotannic acid, ferrous sulphate occasions no change, if free from ferric salt, but produces a white precipitate in a concentrated solution. With ferric chloride tannin produces a bluish-black precipitate of f e r r i c g a l l o t a n n a t e (ink), the color of which is destroyed by boiling or reducing agents. Addition of hydrochloric acid in excess dissolves the precipitate, which is reproduced on adding sodium acetate. Ferric acetate behaves like ferric chloride.

Gallotannic acid gives no reaction with a solution of cupric sulphate, but on adding excess of ammonia it is completely precipitated. The reaction may be employed for its determination. Fehling's solution is reduced by gallotannic acid on heating.

With tartar emetic and soluble salts of lead and bismuth, gallotannic acid yields white insoluble precipitates. With lime-water and with ammoniacal barium chloride it yields a white precipitate, turning blue on exposure.

Gallotannic acid is not precipitated by calcium acetate from a solution very slightly acidulated with acetic acid, and the liquid remains clear even after adding twice its volume of alcohol (separation from tartrates, citrates, oxalates, malates, etc.).

With an ammoniacal solution of potassium ferricyanide, gallotannic acid produces a deep red color changing to brown, even in very dilute solutions. The reaction, which was first observed by the author, is very delicate, but the color is destroyed by a large excess of the reagent. A somewhat similar reaction is produced by gallic acid.[1]

Ammonium molybdate yields with tannin a red coloration,

[1] G. G r i g g i (*Chem. Zeit. Rep.*, 1899, 29), gives the following reaction. Gallic acid in dilute solution gives a bright ruby-red color with potassium cyanide, which disappears on standing, but is reformed on agitating in presence of air or by the addition of hydrogen peroxide. A solution of tannin or pyrogallol gives a yellowish-red color with potassium cyanide, which is more slowly decolorized. The addition of excess of hydrogen peroxide gives a permanent yellow-brown color with gallic acid and a dirty-white precipitate with tannin.

which is yellow in very dilute solutions, and is destroyed on adding oxalic acid.

Gallotannic acid may be determined with considerable accuracy by oxidation with a standard solution of permanganate (page 38).

Gallotannic acid may be extracted from its acidulated aqueous solutions by repeatedly agitating with ethyl acetate free from alcohol, and may thus be separated from tartaric, citric, malic, and other vegetable acids, but not from gallic acid. In the case of ink, sufficient oxalic acid must be added to wholly change the color of the liquid.

Some of the foregoing reactions furnish important distinctions between gallotannic acid and gallic acid and pyrogallol, which in many respects it closely resembles. Others seem to distinguish it from the different varieties of tannin. The table on page 65 shows the reactions of gallotannic and gallic acids and pyrogallol in juxtaposition. The comparative reactions of gallotannic acid and other tannins are given on page 23.

COMMERCIAL GALLOTANNIC ACID is often far from pure. It frequently contains more or less glucose, chlorophyll, volatile oil, and gallic and ellagic acids. Starch has been met with to the extent of 25 per cent., and in more than one instance the author has known it to be entirely substituted by gallic acid, either intentionally or accidentally.

Glucose may be detected by precipitating the solution of the sample with basic acetate of lead, and heating the filtrate with Fehling's solution. A *glucoside* may be detected by the same method, after boiling the solution with dilute sulphuric acid for ten minutes, and neutralizing the liquid with soda.[1]

If *chlorophyll* be present, on shaking the sample with an equal weight of water and the same volume of ether the ethereal layer will be colored more or less greenish.

Gallotannic acid should be wholly soluble in alcohol. If a residue be left it should be examined for *starch*.

[1] According to J. E. S a u l (*Pharm. Jour.*, [3] xvii. 387), a very delicate test for glucose, by which it can usually be detected in samples of commercial tannin, is to agitate about 0.01 gramme of the sample with 3 c.c. water, and then add three drops of an alcoholic solution of thymol. 3 c.c. of concentrated sulphuric acid should then be poured in so as to form a separate layer below the aqueous liquid. Under these circumstances, tannin containing sugar yields a turbid deep rose-colored solution, while gallic acid remains untinted, or merely develops a very faint pink tint in the sulphuric acid layer; and pyrogallol yields a dull violet solution.

Mineral impurities will be indicated by ignition. As a rule, commercial tannin leaves a very insignificant proportion of ash, 0.4 per cent. being apparently the maximum proportion recorded.

Gallic acid may be detected in commercial tannin by leaving the aqueous solution of the sample in contact with a piece of untanned skin, and agitating the liquid from time to time. If the tannin be pure it is entirely absorbed, and the liquid becomes insipid, and no longer gives a coloration with ferric chloride; the contrary being the case if gallic acid be present. Ungummed silk absorbs both tannic and gallic acids, but according to V i g n o n, tannin is much more readily absorbed than gallic acid, and from solutions containing these two in equal quantities, only the tannin is absorbed.

A test which is said to be shorter than the above, and at the same time capable of detecting traces of gallic acid in tannin, has been described by S. Y o u n g (*Chem. News*, xlviii. 31). The sample is dissolved in a little water, ether added equal in measure to about one-third of the water used, and the whole well shaken. On standing, three layers are formed. The ethereal or uppermost is removed, evaporated, and the residue dissolved in water and tested with potassium cyanide, when a strong red coloration will be obtained if the sample contained even a trace of gallic acid. The middle layer contains still more gallic acid, while the lowest aqueous layer is almost free from it. By repeating the agitation with ether several times a complete separation of the gallic acid can be effected.

A determination of the actual *gallotannic acid* present in the commercial article is best made by Löwenthal's permangate method. The residue of "not tannin" does not appear always to consist entirely of gallic acid, glucose being probably present in some cases.[1] The following results were obtained by T. M a b e n (*Pharm. Journ.*, [3], xv. 852), by applying Löwenthal's method to representative specimens of commercial tannin. The *moisture* was determined by drying the samples *in vacuo* over sulphuric acid.[2]

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[1] The author found that commercial tannin varied to the extent of 30 to 40 per cent. in its power of precipitating acetate of lead, which would react with both gallic and gallotonic acids.

[2] According to C. B ö t t i n g e r (*Jour. Soc. Dyers*, &c., July, 1888), even the purest commercial tannin is not a uniform substance. When heated to 150°, under pressure, with concentrated hydrochloric acid, it gives off a gas burning with a

	1	2	3	4	5	6	7	8	9
Moisture, ...	5.0	8.0	5.0	7.0	6.0	7.0	3.0	3.0	4.0
Gallotannic acid, ...	88.8	86.9	54.4	56.9	79.9	77.2	82.3	59.7	70.7
Not-tannin (by difference), . .	6.2	5.1	40.6	36.1	14.1	15.8	14.3	37.3	25.3
$KMnO_4$ required for "not tannin,"	5.86	1.92	6.01	6.94	1.08	3.08	6.63	5.55	3.89

Ellagitannic Acid. $C_{14}H_{10}O_{10}$.

This variety of tannin is contained in divi-divi and myrabolams, and as a glucoside in pomegranate rind. When boiled with dilute acids, or heated with water to 110° C. in a sealed tube, it loses H_2O and yields the anhydride, e l l a g i c a c i d. In its other chemical reactions, ellagitannic closely resembles gallotannic acid, but yields a light brown precipitate with cupric acetate.

Ellagic Acid.

$$C_{14}H_8O_9, \text{ or } C_6H_2(OH)_2 \left\{ \begin{matrix} CO.O \\ O.O \end{matrix} \right\} C_6H_2(OH).CO.OH.$$
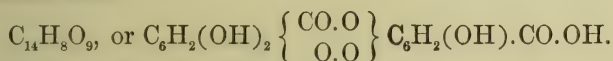
This acid differs in composition from gallotannic acid by two atoms of hydrogen, and is formed when a concentrated aqueous solution of that body fs exposed for a considerable time to the air, or by its reaction with iodine :—$C_{14}H_{10}O_9 + I_2 = 2HI + C_{14}H_8O_9$. Ellagic acid is also produced by the dehydration of ellagitannic acid (see above), and by the action of oxidizing agents on gallic acid. It is a constituent of bezoar stones.[2] Air-dried ellagic acid contains 1 molecule of water, which it loses at 100° and re-absorbs in moist air. When heated to 200° C. it loses H_2O, and forms an a n h y d r i d e, $C_{14}H_6O_8$, which is slowly reconverted into ellagic acid by boiling with water. When pure, ellagic acid forms a

green-edged flame (methyl chloride); and on heating the tannin with water and excess of bromine, small quantities of products volatile with steam are produced. Nevertheless such tannin is almost completely fixed by hide, and yields nothing but gallic acid when boiled with aqueous caustic alkalies. When boiled with a mixture of phenylhydrazine hydrochloride and sodium acetate it becomes intensely yellow, changing to a brownish-yellow coagulated mass on standing. This reaction is not caused by the presence of a sugar.

[1] Ellagic acid is readily prepared by pouring a concentrated alcoholic extract of divi-divi into water. The precipitate may be purified by crystallization from hot alcohol. It may also be obtained by boiling the aqueous extracts of divi-divi, myrabolams, pomegranate rind, &c., with dilute hydrochloric acid, and may be purified by solution in alcohol. It may also be prepared by heating gallic acid with dry arsenic acid to 160° C., but the product is difficult to purify from arsenic. It may be obtained from bezoar stones (intestinal concretions of a Persian species of goat) by boiling with potash and precipitating with hydrochloric acid.

sulphur-yellow crystalline substance, nearly insoluble in water, even when boiling, and but little soluble in alcohol. The aqueous and alcoholic solutions have an acid reaction. It is but slightly soluble in ether, but small quantities may be effectually extracted from the aqueous solution by agitation with that solvent. In caustic potash ellagic acid dissolves with yellow color, which rapidly becomes darker, and black crystals of potassium glauco-melanate separate. Neutral ferric chloride, when shaken with solid ellagic acid, is colored greenish at first, but afterwards becomes inky black. The solution of ellagic acid in hot alcohol has a pale yellow color, and deposits the acid in sulphur-yellow crystals on cooling. With lead acetate ellagic acid yields a precipitate containing 63 per cent. of PbO. Ellagic acid dissolves in fuming nitric acid with deep crimson coloration. With the product from divi-divi, the nitric acid solution retains its crimson color on dilution with water, but when derived from other sources, dilution is said to change the color to orange.

Caffetannic Acid. Caffetannin. $C_{14}H_{16}O_7$.

This variety of tannic acid occurs in coffee berries. When isolated it forms brittle masses or a yellowish-white powder. It is only slightly soluble in ether. On boiling caffetannic acid with dilute sulphuric acid, or by exposing its solution in caustic alkali to the air, the liquid acquires a bluish-green color owing to the formation of the oxidation-product v i r i d i c a c i d. This body is characterized by giving a blue precipitate with lead acetate, and a crimson color with strong sulphuric acid. On prolonged boiling with caustic alkalies, caffetannic acid yields c a f f e i c a c i d, $C_9H_8O_4$, which crystallizes from the neutralized solution. When fused with caustic potash, caffetannic acid yields protocatechuic and acetic acids. Heated alone, it gives catechol. Ferric chloride gives a dark green color with caffetannic acid, and cinchonine sulphate a white precipitate, but solution of gelatin is not affected.

Quercitannic Acid. Quercitannin.[1]

According to C. E t t i (*Jour. Chem. Soc.*, xliv. 994) the tannin of oak-bark exists in two forms, namely, as q u e r c i t a n n i c a c i d, and as an anhydride of that acid, or p h l o b a p h e n e.[2]

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[1] Quercitannic acid is said to be identical with the tannins of the elm, willow, and black tea.

[2] Quercitannic acid may be prepared from treating oak-bark with alcohol, evaporating the filtered liquid, dissolving the extract in water, and agitating the solu-

Quercitannic acid is not a glucoside, the reactions which formerly caused confusion being really due to the presence of l æ v u l i n, which on treating the oak-bark with dilute sulphuric acid was converted into lævulose.[1]

Quercitannic acid is amorphous, brownish-red, and readily soluble in water and alcohol. When pure, it dissolves completely in ethyl acetate, and does not yield anything to pure ether or benzene.

In very dilute alcoholic solution, quercitannic acid yields a pure yellow precipitate with neutral or basic acetate of lead, but in aqueous solution the precipitate produced is light brown. With ferric and ferroso-ferric salts quercitannic acid gives a blue-black color, and yellowish-white precipitates with tartar-emetic, gelatin, albumin, and alkaloids. It is also precipitated by solution of lead nitrate, ammoniacal chlorides of zinc and magnesium, ammoniacal sulphate and acetate of copper, and by molybdate of ammonium. It readily reduces permanganate and Fehling's solution. According to H. R. Procter, a dilute solution of quercitannic acid does not precipitate blood-albumin, and in addition renders it uncoagulable by heat, even in presence of free acid.

According to E t t i, quercitannic acid has the composition $C_{17}H_{16}O_9$.[2] At 130° to 140° it gives up water and yields the first

tion with acetic ether. The product obtained on separating and evaporating the ethereal layer is contaminated by a brownish-green terpene resin and with some of the anhydrides of the tannin. The resin may be removed by treating the dried extract with ether or benzene, in which it is readily soluble; and the phlobaphenes or tannin-anhydrides may be separated by dissolving the tannin in ether-alcohol, or partially by mere solution in cold water. Or the soluble anhydrides may be precipitated by saturating the aqueous solution of the alcoholic extract with common salt before shaking with acetic ether.

[1] Tannic acids, which are almost insoluble in water, do not occur in combination with a sugar, and are therefore not glucosides; their basis is said to be a ketone acid, gallylgallic acid, having the constitution :—

$$C_6H_2 < \frac{(OH)_3}{CO} - C_6H < \frac{(OH)_3}{COOH}$$
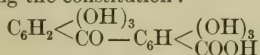
and is formed from two molecules of gallic acid with the elimination of one molecule of water.

[2] Etti points out the following distinctions between gallotannic and quercitannic acids :—

	Gallotannic Acid.	Quercitannic Acid.
Heated with dilute sulphuric acid to 140° under pressure,	Yields gallic acid, giving a white precipitate with lead acetate.	Yields phlobaphene or oak-red, giving a brown precipitate with lead acetate.
Heated with acetic anhydride,	Forms aceto-tannins.	Yields anhydrides and acetylised anhydrides.
Boiled with aqueous ammonia in an atmosphere of hydrogen,	Yields gallamide and ammonium gallate.	Yields indefinite resinous products.

anhydride or p h l o b a p h e n e, $C_{34}H_{30}O_{17}$, which is brownish-red, nearly insoluble in water and in ether, but readily soluble in alcohol of all strengths. It exists in the original bark together with quercitannic acid, and gives a brownish-red precipitate with lead acetate. When boiled with dilute sulphuric or hydrochloric acid, the phlobaphene loses 1 molecule of water and yields a s e c o n d a n h y d r i d e, $C_{34}H_{28}O_{16}$, from which a t h i r d, $C_{34}H_{26}O_{15}$, may be obtained. All these anhydrides are soluble in alcohol and caustic alkalies, and are precipitated blue-black by ferric chloride. Löwe has obtained a f o u r t h a n h y d r i d e, $C_{34}H_{24}O_{14}$, which he designates o a k-b a r k r e d, a name which has been applied by other observers to the first and second anhydrides.

Tanners designate the anhydrides simply as " coloring matter," and reject barks containing a large proportion, as they impart too red a color to the leather.

From the number and mode of formation of these anhydrides, together with the evolution of methyl chloride on heating the tannin under pressure with dilute hydrochloric acid, Etti concludes that quercitannic acid is a methyl-derivative of digallic or gallyl-gallic acid. Etti also investigated a tannic acid of the formula $C_{20}H_{20}O_{9}$, obtained from the bark of a different species of oak. This agreed with the other acid in all its properties, except that it gave a bluish-green color with ferric chloride, rapidly changing to deep green, and on addition of sodium carbonate first to blue and then to red. This variety of tannin yields four anhydrides similar in character to those of the acid with 17 atoms of carbon.

L ö w e (*Jour. Chem. Soc.*, xl. 901) gives $C_{28}H_{26}O_{15}$ as the formula of the hydrated tannic acid of oak-bark, and $C_{28}H_{22}O_{11}$ as that of the oak-red. B ö t t i n g e r (*Ber.*, xvi. 2710) adduces evidence of weight in favor of $C_{19}H_{16}O_{10}$ as the formula of the tannic acid, and $C_{38}H_{26}O_{17}$ as that of the oak-red. He has also attributed to the latter the formula $(C_{14}H_{10}O_{6})_{2}H_{2}O$ (*Jour. Chem. Soc.*, xxxviii. 650). To the tannin of oak-*wood* he attributes the formula $C_{15}H_{12}O_{9}$ (*Jour. Chem. Soc.*, lii. 584).[1]

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[1] It is probable that the discrepant statements respecting the composition of oak-bark tannin are due to the presence of two analogous bodies. According to F. M u s s e t (*Jour. Soc. Chem. Ind.*, iii. 525), this is actually the case, both tannins being precipitable by gelatin and oxidizable by permanganate. One, which he terms o a k - t a n n i n, may be extracted by repeatedly agitating the infusion with acetic ether, in which the o a k - r e d t a n n i n is insoluble. He prefers, however, to determine the oak-red tannin by precipitation with iodine, avoiding presence of air. The compound formed contains 7.8 per cent. of iodine and an equal quantity

According to Etti, the most of the sparingly soluble ketone tannic acids occur in plants in combination with a metallic base, probably magnesium. By concentrating the aqueous extract and precipitating with hydrochloric acid, and purifying the resulting tannic acid by extracting with alcohol and ether, he has succeeded in isolating acids of the following composition:—

$C_{16}H_{14}O_9$ from the stalk oak,

$C_{18}H_{18}O_9$ from tannery oak-bark,

$C_{20}H_{22}O_9$ from copper beech-bark,

$C_{22}H_{26}O_9$ from hop-cones.

That the first acid contains a ketone group is proven by the formation of a phenylhydrazine derivative and an oxime. From a consideration of its reactions, Etti ascribes to it the formula:—
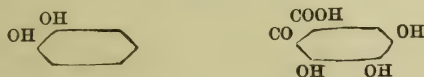
with two methoxy-groups of unknown position.

Animal Tannin.

A body having the character of a tannin has been extracted from corn weevils (*Chem. News*, lvi. 175). Three per cent. was obtained of a substance forming small reddish-yellow scales soluble in water, alcohol, aqueous ether, etc., and precipitating gelatin, albumin, and alkaloids. It gave a bluish-black coloration with ferric salts, and on boiling with dilute sulphuric acid split up into glucose, gallic acid, and a red phlobaphene.

Lupulotannic Acid. Hop-Tannin. $C_{24}H_{24}O_{13}$.

The tannin of hops is a glucoside which is easily soluble in water and proof spirit, but not in ether. It gives a green color

of iodine is converted into hydriodic acid. An equal quantity of the infusion is treated with zinc oxide, and, after twenty-four hours, and the absence of more than traces of tannin in the filtered solution being proved by gelatin and ferric acetate, the n o n - t a n n i n m a t t e r s are titrated with a decinormal solution of iodine. By deducting the amount of iodine, required by the non-tannin matters from that consumed by an equal measure of the original infusion, the iodine which has reacted with the tannins is found, and by subtracting from this twice the quantity of iodine contained in the precipitate of iodized oak-red tannin, the iodine corresponding to the oak tannin is ascertained. Examined in this manner, M u s s e t found German oak-barks to contain from 7 to 8 per cent. of oak-tannin, and 6 to 10 per cent. of oak-red tannin.

with ferric salts, a dirty green precipitate with cupric sulphate, a yellow with lead acetate, and a brownish-yellow precipitate with lime-water. It reduces Fehling's solution. Lupulotannic acid yields a precipitate with albumin but not with gelatin, unless it be previously dried at 100° C., by which treatment it is converted into the anhydride or p h l o b a p h e n e, $C_{50}H_{46}O_{25}$, a body coexisting with lupulotannic acid in the hop, and having all the characteristics of a tannin. According to E t t i, it is a glucoside which yields protocatechuic acid, phloroglucin, and glucose. It precipitates gelatin solution completely, and reduces Fehling's solution. It is soluble in alcohol and in alkalies, and is precipitated on acidulating the latter solution.

Catechu-tannic Acid. Mimotannic Acid.

The tannins which yield catechol when heated differ from the pyrogallol derivatives by giving a green reaction with ferric acetate. Like oak-bark tannin, they give insoluble red phlobaphenes or anhydrides by the action of dilute acids. Their constitution is in most cases only very imperfectly understood, and even the composition of them is uncertain. The tannin of catechu is typical of this class of tannic acids.

Catechu-tannic acid, probably identical with the body described as m i m o t a n n i c a c i d, is the astringent substance contained in catechu (cutch) and gambier.[1] It is extracted by cold water from catechu, and is also formed by heating catechin alone to 130°, with water to 110°, or by boiling it with alkalies. Catechu-tannic acid is a dark reddish-brown powder, moderately soluble in water, insoluble in ether, but readily soluble in alcohol and in acetic ether. It resembles gallotannic acid in many of its characters, but gives a greyish-green precipitate with ferric salts, and no reaction with ferrous salts. It is also distinguished from gallotannic acid by giving a dense precipitate with cupric sulphate and none with tartaremetic; and by yielding catechol and phloroglucol by fusion with potash. The aqueous solution is precipitated by gelatin, albumin, and dilute sulphuric acid. When treated with hydrochloric acid and potassium chlorate in excess, catechu-tannic acid yields a chloro-substitution-product which is turned purple-red by sodium sulphite. Catechin gives the same reaction.

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[1] It is doubtful whether the tannin of gambier is strictly identical with that of catechu.

Catechins.

Catechu and gambier contain from 20 to 30 per cent. of a body called c a t e c h i n, which appears to be the type of a number of similar bodies occurring in all or most tannin materials yielding catechol-tannins. A catechin has certainly been recognized in Colorado quebracho, and the kinoïn of kino is a body of similar nature. The co-existence of several homologous or closely analogous bodies of the nature of catechin, even in catechu itself, is the probable explanation of the difference in the formula assigned to catechin by different observers. Unless qualified in some way, by the term c a t e c h i n the body contained in catechu (cutch) or gambier is always understood.

CATECHIN may be prepared from gambier or catechu by digesting the powdered substance in cold water to remove the catechu-tannic acid, and exhausting the residue with boiling water. Impure catechin deposits as the solution cools, and may be redissolved in boiling water and decolorized by animal charcoal.

Catechin forms a white powder consisting of silky crystalline needles. It melts at 217° C. and yields a sublimate of catechol on further heating. It dissolves readily in alcohol and boiling water, but requires 1133 parts of cold water for solution. Agitation with ether or acetic ether extracts it from its aqueous solution, a fact which may be utilized for its purification. Though sometimes called c a t e c h u i c a c i d, catechin possesses no acid properties, though it is soluble in alkalies. The alkaline solution turns brown on exposure to air. Catechin dissolves in strong sulphuric acid with deep purple coloration. The aqueous solution gives white precipitates with lead acetate and mercuric chloride, and reduces ammonio-nitrate of silver, but, unlike the tannins, does not precipitate gelatin, alkaloids, or tartar-emetic; on the other hand, it yields a precipitate with albumin. It is oxidized by permanganate in presence of free acid, a fact which may be utilized for its estimation (page 73). Heated under pressure to 140° with dilute sulphuric acid, catechin yields catechol and phloroglucol. With diazobenzene chloride, catechin gives a red crystalline precipitate, which is soluble in alcohol and ether, and dyes wool golden-brown.

Catechin is often described as an anhydride of mimotannic acid, the tannin of catechu and gambier, but according to E t t i the opposite of this is probably the case. In constitution, catechin is probably a phloroglucide of tetra-hydrogenized protocatechuic acid. This view accounts for its decomposition by fusing caustic

alkali with evolution of hydrogen and formation of protocatechuic acid and phloroglucol:—$C_6H_7.COOH:2C_6H_3(OH)_2 + 4H(OH) = C_6H_3(OH)_2.COOH + 2C_6H_3(OH)_3 + 2H_2$.

Different observers, however, are not agreed as to the composition of catechin. Thus Liebermann and Tauchert, who prepared a crystallized diacetyl-derivative, attribute to catechin from catechu the formula $C_{21}H_{20}O_9 + 5H_2O$ (*Jour. Chem. Soc.*, xl. 53.)

By the graduated action of heat or dilute acid on catechin it may be successively converted into the following anhydrides:—

Catechin,	$2C_{19}H_{18}O_8 = C_{38}H_{36}O_{16}$	{ Not acid; does not precipitate gelatin.
Catechin-red; Catechu-tannic acid,	} $C_{38}H_{34}O_{15}$	} Acid; precipitates gelatin.
Di-anhydride,	$C_{38}H_{32}O_{14}$	
Tri-anhydride,	$C_{38}H_{30}O_{13}$	
Catechuretin,	$2C_{19}H_{14}O_6 = C_{38}H_{28}O_{12}$	} Insoluble in water.

KINOÏN, $C_{14}H_{12}O_6$, a body resembling catechin, is obtained from green or Malabar kino by boiling with dilute hydrochloric acid, decanting from the precipitated k i n o - r e d, and agitating with ether. When recrystallized from hot water it forms small colorless prisms, which are difficultly soluble in cold water but readily in hot water and in alcohol. Its solution is colored red by ferric chloride. Heated to 120°–130° it yields the anhydride, k i n o - r e d, $C_{28}H_{22}O_{11}$, and this when heated to 160°–170° gives $C_{28}H_{20}O_{10}$. Both anhydrides are precipitated by gelatin, but kinoïn itself is not. When heated with hydrochloric acid to 120°–130°, kinoïn yields methyl chloride, gallic acid, and catechol, and hence probably has the constitution of a g u a i a c o l or m e t h y l - c a t e c h o l g a l l a t e.

According to Hennig kino-red is a coloring matter in intimate combination with a tannic acid supposedly identical with gall-tannin. As it possesses acid properties, kino-red has been termed *kinoic-acid*.

Kino is quite extensively employed in medicine, as it is a powerful astringent, for the purpose of suppressing morbid discharges.

Tannin-yielding Materials.

The following table gives the common names of the principal tannin-yielding substances used in commerce, together with the botanical names of the plants producing them, the parts of the plant used, and the usual percentage of tannin contained in good specimens of each material:—

Common Name of Material.	Botanical Name of Plant.	Part of Plant used.	Ordinary per cent. of Tannin.
Oak-bark, ...	Quercus pedunculata and Q. robur.	Bark.	8–13
Cork-bark, ...	Quercus suber.	Inner bark.	10–14
Valonia, ... , .	Quercus ægilops.	Acorn-cups.	25–35
Chestnut-oak extract, ...	Quercus (an American species).	Extract from bark.	20–25
Hemlock-bark, . . .	Abies Canadensis.	Bark.	10–14
" extract, .	Abies Canadensis.	Extract from bark.	18–28
Churco-bark, ...	Oxalis gigantea (Chili) ?	Bark.	26
Monesia-bark, . . .	Chrysophyllum glycyphlœum.	Bark.	32
Mangrove-bark, .	Rhizophora mangla.	Bark.	9–33
Alder-bark, ...	Alnus glutinosa.	Bark.	16
Larch-bark, ...	Abies larix.	Bark.	6–8
Mimosa (Wattle), .	Acacia dealbata and A. molissima.	Bark.	24–30
Catechu (Cutch), .	Acacia and Areca catechu.	Extract from wood.	45–55
Gambier, ...	Uncaria gambir and U. acida.	Extract from leaves and small branches.	36–40
Sumac, ...	Rhus coriaria, R. cotinus, &c.	Leaves.	15–30
Chestnut-wood, .	Castanea vera.	Wood.	8–10
" extract,	Do.	Extract from wood.	14–20
Quebracho-wood,	Aspidosperum quebracho, &c.	Wood.	14–23
" extract, solid,	Do.	Extract from wood.	53–60
" " liquid,	Do.	Do. do.	36
Marsh Rosemary,	Statice coriaria.	Root.	20–24
Ratanhia, ...	Krameria triandria.	Root.	38–42
Myrabolams, . . .	Terminalia chebula and T. belerica.	Fruit.	20–40
Divi-divi, ...	Cæsalpina coriaria.	Pod.	30–50
Kino, ...	Pterocarpus marsupium, and Drepanocarpus senegalensis.	Extract from fruit.	75
Gall-nuts, ...	Quercus infectoria, &c.	Galls.	60–77
Tamarisk galls, . .	Tamarix Indica, and T. Africana.	Galls.	50–54
Rove, ...	? (Greece and Asia Minor).	Galls.	24–34

C. C o u n c l e r (*Jour. Chem. Soc.* xlviii. 946) has published the following results.[1] The method of analysis is not stated, but was probably von Schroeder's modification of Löwenthal's process.

	Moisture.	Tannin.	
		Total.	Readily Soluble.
Mimosa-bark, Tasmania, ...	11.35	16.88	15.05
" "	8.25	23.12	19.93
" Victoria, ...	11.75	21.20	16.54
" "	9.25	17.30	12.70
Root-bark of Kermes Oak, "Garouille" (*Quercus coccifera*), ...	10.00	8.69	7.88
Birch-bark, Friedrichsruh, ...	. .	4.97	3.98
Alder-bark, Riesenthal, ...	18.00	11.68	11.15
" "	10.70	7.38	5.35
" "	6.80	8.17	6.02
" "	10.50	12.53	11.82
" "	11.67	11.15	8.93
Willow-bark, Russian, *Salix purpurea*, ...	7 8	1.72	0.86
" " *viminalis*, ...	7.9	3.42	2.14
" " *purpurea*, ...	8.7	4.71	2.70
" " *capsica*, ...	13.4	2.62	1.34
" " *amygdalina*, ...	7.6	3.17	2.27
Quebracho-wood (highest), ...	11.3	19.36	10.97
" (lowest), ...	10.0	16.42	7.66
Chestnut-wood, ...	7.3	8.49	5.48

[1] In the same paper C o u n c l e r gives some interesting calculations of the

The following results by K a y and B a s t o w (*Jour. Soc. Dyers and Col.*, iii., 132) were obtained by the assay of tanning materials exhibited in the Indian and Colonial Exhibition of 1886. The process employed was Procter's modification of Löwenthal's method (see page 73).

Tanning Material.	Percentage of Tannin.	
	In terms of Oxalic Acid.	In terms of Gallotannic Acid.
Terminalia tomentosa (galls), ...	9.24	6.53
" belerica (fruit), ...	12.86	8.48
" chebula (fruit), ...	52.65	34.49
Ceriops Rosburghiana (bark), ...	37.65	24.66
Camia auriculata, ...	19.94	12.86
Acacia catechu (extract), ...	76.00	. .
" " (bark), ...	21.35	. .
" arabica (pods), ...	22.44	. .
Areca catechu (nuts), ...	14.28	. .

The results of the assay of a large number of tannin matters by P r o c t e r' s method are given on page 73.

F. S i m a n d (*Jour. Soc. Chem. Ind.* iii., 574) gives the following results of the assay of various tannin extracts by the Löwenthal-Neubauer method.

Extract from	Density, Beamé.	Tannin.		Remarks.
		Total.	Soluble in Cold Water.	
Quebracho-wood, solid, .	. .	73.08	70.09	Dried before analysis.
Valonia, solid, ...	. .	70.44	68.59	Do.
Oak-wood, liquid, ...	13°	14.47	15.09	Do.
Oak-bark, liquid, ...	32°	24.37	23.72	Commercial extract.
Fir, liquid, ...	32°	14.31	13.72	Do.
Chestnut-wood, liquid, . .	31°	23.52	22.68	Do.
Sumac, liquid, ...	34°	13.38	10.75	Do.

price per kilogramme of the tannin present in various commercial extracts. Thus:—

Material.	Price per 100 kilos. in shillings.	Percentage of tannin.	Price of tannin per kilogramme (=2.19 lbs.) in pence.
Quebracho-wood, ...	16–18	16–19	11
" " extract, .	16–18	36–60	14–18
Hungarian pine-bark, . . .	11	12	12
" " extract, . .	43	14	36
Oak-bark extract, ...	55	. . .	38
Chestnut-wood, ...	8	8½	11
Sumac extract, ...	92	11	54

I. I s h i k a m a has published the following figures showing the strength, in terms of gallotannic acid, of various tannin-yielding materials of Japanese origin (*Chem. News*, xlii. 274).

	Percentage of Tannin (in terms of Gallotannic Acid).
Gall-nuts (Japanese), ...	. 58.8 to 67.7
" (Chinese), ...	. 77.4
Fruit of *Alnus firma*, ...	. 25.3 to 27.5
Bark of *Myrica rubra*, ...	. 10.5 to 15.0
Rind of Pomegranate, ...	. 20.4
Betel-nut, ...	. 18.0
Oak-bark (*Quercus dentata*) (inner), ...	7.4
" " (outer), ...	2.6

D. H o o p e r (*Amer. Jour. Pharm.* 1894, 377) has examined a large number of Indian tannin-yielding plants for the amount of tannin which they contain. The following table gives a summary of his results:

	Per cent. Tannin.		Per cent. Tannin.
Bridelia montaria	. 39.4	Mangifera indica	. 16.7
Acacia pycriantha	. 33.8	Eugenia arnottiana	. 16.1
Acacia decurrens	. 33.4	Terminalia arjunn	. 16.0
Terminalia chebula	. 31.0	Anogeissus latifolia	. 15.5
Psidium Guejava	27.4	Dioxpyrus embryopteris	. 15.0
Candelia Rheedii	27.4	Saxifraga ligulata	. 14.2
Acacia Melarioxylon	. 26.8	Ficus racemosa	. 14.1
Acacia leucophloea	. 20.8	Myrica nogi	. 13.7
Woodfortia floribunda	. 20.6	Cassia fistula	. 12.9
Acacia arabica	. 25.5	Diospyrus (fruit)	. 12.4
Cassia auriculata	. 20.7	Eugenia Jarubal	. 12.4
Rhodomyrtus tomentosa	. 19.5	Eugenia Jarubolana	. 12.0
Macaranga Ronburgi	. 18.4	Eugenia montana	. 11.9
Casuarina equisetifolia	. 18.3	Ficus indica	. 10.9
Cicca distichia	. 18.1	Mimusops hexandra	. 10.3
Phyllanthus Emblica	. 18.0	Flueggia leucophloea	. 10.3
Acacia dealbata	. 17.8	Eugenia caryophyl-lifolia	. 10.1
Terminalia belerica	. 17.4	Mimosa pudica	. 10.0
Bassia longifolia	. 17.7		

C ATECHU or C UTCH is the dried extract from the wood of the *Acacia catechu* and allied species. It is very similar in nature to gambier. C u t c h, however, produces a hard red leather-like *Mimosa,* and generally occurs in more or less brittle, splintery masses. G a m b i e r occurs in light, porous brown cubes, more or less adherent, or in blocks measuring 2 feet × 1 foot × 9 inches, soft internally and wrapped in matting. *Terra japonica* is a trade-name, now somewhat obsolete, for both cutch and gambier.

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In addition to a large proportion of a variety of tannin (catechu-tannic acid), catechu contains 30 or 40 per cent of c a t e c h i n (page 45), which is deposited on cooling a boiling aqueous solution.

Catechu is not infrequently adulterated ; starch, sand, clay, and blood being among the materials employed for the purpose, and Jessart states he has met with an admixture of 60 to 70 per cent. of ferrous carbonate.   Catechu should not yield more than 5 per cent. of *ash*, nor contain more than 12 per cent. of matter insoluble in boiling alcohol.   *Starch* may be detected by treating the sample with alcohol, boiling the insoluble residue with water, and testing the cold liquid with iodine, which gives the well-known blue color in presence of starchy matters.   The presence of *ordinary tannin-matters* is indicated by the modified color which the sample gives with ferric salts, pure catechu giving a decided green. *Blood* may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and most offensive vapors will be produced.   Aqueous solution of catechu should give with albumin or gelatin an abundant precipitate; with salts of tin and lead, yellow precipitates of various tints; and a brown precipitate with bichromate of potassium.   It should take a decided brown hue with alkalies, and give a greenish color with ferric chloride.   Good catechu yields at least half of its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catechin on cooling.   Catechu does not wholly dissolve in cold water unless it has been previously modified by age or exposure to dampness.

An aqueous solution of *Pegu* cutch gives dense precipitates with bromine-water and cupric sulphate, neither of which reagents affects gallic, gallotannic, or pyrogallic acid.   In dilute solution, Pegu cutch does not precipitate potassium bichromate, but gallotannic acid does.

The proportion of t a n n i c   a c i d in catechu is best determined by Löwenthal's gelatin-permanganate process (page 73).   The proportion of c a t e c h i n may be roughly deduced from the volume of permanganate decolorized after removal of the mimotannic acid by means of gelatin.   More accurate results are obtainable by employing a moderate excess of gelatin, removing the catechin from the filtrate by agitation with ether, evaporating the ethereal liquid, dissolving the residue in warm water and titrating with permanganate.

In order to distinguish between catechu and gambier, D i c-
t e r i c h (*Pharm. Central.*, H. 1896, 855) recommends the follow-
ing fluorescence test: 3 grammes gambier are dissolved in 25 c.c.
normal caustic potash and 100 c.c. water.   50 c.c. benzene (sp. gr.
0.700) are then added, and the whole is agitated in a separating
funnel.   After allowing to stand, the layers separate, and it is seen
that the benzene shows a more or less intense green fluorescence
according to the duration of the action.   Acacia catechu does not
show this reaction.

KINO generally occurs in irregular black fragments, but it is also
met with in round cakes.   Thin slices are often transparent and
of a reddish color; the powder is red.   Kino should be completely
soluble in hot water, forming a red liquid which gradually becomes
turbid.   Kino is sometimes adulterated, the usual sophistications
being dragon's blood, pitch, catechu, and ratanhia extract.   The
last substance may be distinguished from kino by touching a frag-
ment of the sample with the tongue; kino remains reddish-brown,
but ratanhia extract takes a fine bronze tint, which lasts as long as
the surface of the fragment is wet.   The ash of kino should not
exceed 3 or 4 per cent.

DIVI-DIVI is composed of the bean-like pods of *Cæsalpina cor-
iaria*, a small tree found in the neighborhood of Maracaibo and
other parts of South America.   The pods are about three inches
long, brown or blackish in color, and generally folded up or bent
into the shape of a letter S.   The best pods are thick and fleshy,
and of a comparatively pale color.   Deep brown pods with black
patches have been gathered when wet, or subsequently exposed to
dampness, which injures them considerably.

GALLS is a generic name applied to those excrescences on plants
produced by the punctures of insects for the purpose of depositing
their eggs.   Galls are the most valuable and important of all tan-
nin matters.[1]   *Nut-galls, oak-galls, Aleppo or Turkey-galls* are the
produce of the female of an insect called *cynips* (gall-wasp), which
pierces the buds on the young branches of the *Quercus infectoria*
and other species of oak.   The eggs therein deposited soon hatch,
while the bud loses its natural growth and swells out to the size
of a hazel-nut.   When perfect, the insect punctures a hole and

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[1] A sample of gall-nuts analyzed by Guibourt contained:—tannic acid, 65.0;
gallic acid, 2.0; ellagic and luteo-gallic acid, 2.0; chlorophyll and volatile oil,
0.7; brown extractive matter, 2.5; gum, 2.5; starch, 2.0; woody fibre, 10.5;
sugar, albumin, and ash, 1.3; water, 11.5 per cent.

escapes.   Good gall-nuts should not be so pierced; they should be heavy, and of a fresh green or blue color ("green galls"). If the insect has escaped, they are yellow and inferior ("white galls"). The best oak-galls contain 60 to 70 per cent. of gallotannic acid, and about 3 per cent. of gallic acid.

Worm-eaten galls are sometimes doctored by filling the holes with wax. The fraud may be detected by immersing the galls in boiling water, which melts the wax and renders the holes visible. Exhausted galls are occasionally colored by washing them with a solution of ferrous sulphate, which is readily detected by its chemical reactions.

Knoppern are galls formed from immature acorns of several species of oak, and are largely used for *tanning* throughout Austria. In a large number of samples of Austrian galls of the year 1884, Eitner found from 28 to 35 per cent. of tannin, the moisture being about 12 per cent. (*Jour. Chem. Soc.*, xlviii. 947).

Chinese and *Japanese gall-nuts* are a production of the *Rhus semialata*. They are very light and hollow, and distorted by numerous protuberances, and are completely covered by a thick velvety grey down. Chinese galls are much used for the preparation of tannin, of which they contain about 70 per cent. English galls from the common oak are much inferior to the foreign varieties. They are smooth, brown, and slightly speckled with pale brown excrescences. The Japanese are smaller, paler, and generally more esteemed.

MYRABOLAMS are the fruit of several species of *Terminalia*. In size and shape the myrabolam resembles a slightly shriveled plum. As imported, myrabolams contain from 3 to 7 per cent. of moisture, and leave about 10 per cent. of ash on ignition. The tannin is chiefly contained in the dried pulp enclosing the stone.

Good myrabolams should be of a pale buff color, plump, or but slightly shriveled, and free from worm-holes or blackish stains or blotches. They should be hard and firm, and when broken with a hammer should form a light-colored dry powder and irregular fragments. If they crumble between the fingers to a dark colored dust, or flatten under the hammer, they are inferior. The stones contain very little tannin, and hence their proportion should be ascertained by breaking 50 nuts with a hammer, clearing the stones from any adherent pulp, and weighing them separately. They may constitute from 23 to 52 per cent. of the whole fruit.

Ground myrabolams should be light in color, dry, and free from

a saline or an intensely bitter taste.   When slightly moistened and rubbed in the hand they should adhere very tenaciously to the skin.

Myrabolams are sometimes mixed with earth, sand, *nux vomica*, betel-nuts, and a variety of seeds and berries.   They may also be adulterated with finely-ground divi-divi, wild galls, and old and worthless sumac.   On scattering the powdered substance on a sheet of paper, and examining it with a lens, it will be recognized by the fragments of its brown, flat, smooth pea-like seeds, which from their hardness and smoothness, escape being crushed to powder.   The leaf stalks of sumac are readily distinguished from the torn, irregular fibre of the myrabolams.

Myrabolams contain the same tannin principles as Algarobilla, and in similar ratio.

Sumac, or Shumac, consists of the leaves, leaf-stalks, and small twigs of several species of *Rhus*.   It is sometimes sold whole, sometimes coarsely bruised, but more commonly in fine powder. The best Silician sumac gives a bright green powder which has a pleasant tea-like odor.   The second quality is reddish-yellow; and Spanish sumac has usually a fawn-color.

Sumac should be quite dry, and free from cakes or lumps, the presence of which shows the sample has been exposed to dampness and will probably have become seriously deteriorated.   The color should be bright.   If dull, the sample is probably damaged by long keeping, or is mixed with sumac of inferior quality.

Sumac sometimes contains a notable proportion of earth or sand; 10 per cent. of ash is sometimes left on ignition.

Valonia consists of the acorn-cups of certain species of oak, chiefly exported from Smyrna, but also obtained from other parts of Asia Minor, as well as from Greece and the Grecian Archipelago.   They should be of a bright drab color.   If dark they have suffered from dampness, and will be deteriorated in quality.

Cayota is a reddish-brown bark which comes from the southern part of Mexico, where it is used for tanning thick sole leather. It is easily powdered, has a resinous odor, and contains from 22–30 per cent. tannin.   It is said to give silk the same suppleness as when sumac is used.

Algarobilla consists chiefly of the pods of the *cæsalpinia brevifolia* of Chili; it is used considerably in its native country for tanning and black dyeing.   Its tannin is not a uniform body, but is a mixture of two, one of which is a glucoside of gallotannic acid, furnishing gallic acid and sugar by hydrolysis.   The second tan-

nin, present in much larger quantity, is free from sugar. It easily separates into ellagic acid, and is identical with the tannic acid prepared from myrabolams and divi-divi.

Algarobilla gives the following reactions:

Sulphuric acid
Hydrochloric acid } —render the solution turbid.
Oxalic acid

Caustic alkalies—liquid turns brown, slight precipitate.

Lime water—darker color with an abundant dirty white precipitate.

Alum
Stannous chloride } —clear yellow-brown precipitate.

Aluminium acetate—copious clear yellow precipitate.

Lead acetate—greenish-yellow precipitate.

Copper acetate—reddish-brown precipitate.

Iron salts—blacken liquid; bluish-black precipitate.

Iron salts (in small quantity)—greenish-black color.

Potassium bichromate—liquid yellowish-brown.

Gelatin—copious yellow-brown precipitate.

CANAIGRE consists of the ground roots of the *rumex hymenosepalum*, growing in the sandy soils of Mexico and the southwestern states of America. The wood contains 20–30 per cent. of tannin, and its extract contains 40–60 per cent. of tannin. (Trimble.)

QUEBRACHO is a tree which is native of Argentina, Cuba, and other sub-tropical countries. Its name signifies "break hatchet," and refers to the great hardness of the wood. The tree grows to a considerable size, and its bark is thick and red and possesses important tanning properties. The wood has a density of 1.26, and when freshly cut has a bright orange color which rapidly darkens to a reddish shade on exposure. The tannin from the bark and wood is readily extracted by boiling water. The ground wood contains about 18 per cent. of tannin, which, however, is reduced on exposure to the air for any length of time, probably due to a resinification setting in. The extract, 30° Be., contains about 50–56 per cent. of tannin, while the dried extract will contain over 60 per cent. of tannin.

An infusion of quebracho gives the following reactions:—

Dilute sulphuric acid and hydrochloric acid, a bright orange precipitate.

Alum to an alkaline solution, an orange-red lake.

Aluminium acetate, a yellow precipitate.

Stannous chloride, an orange-yellow precipitate.

Stannic chloride, a darker precipitate.

An iron salt, in small quantity, a blue-black precipitate.

An iron salt, in large quantity, a grey precipitate.

Potassium bichromate, a reddish-brown precipitate.

Copper salts, a greenish precipitate.

Lead acetate, a bright precipitate.

Aluminium sulphate, a greyish precipitate.

PALMETTO is an evergreen palm-like shrub, which grows abundantly in the Southern States of America. The extract contains from 8 to 12 per cent. of tannin and is employed for tanning leather.

Qualitative Recognition of Tannin Materials.

The table on next page, due to H. R. Procter, shows the behavior of infusions of a number of commercial tannin matters with various reagents. The infusions must be very weak, not exceeding 1.002 in specific gravity, or precipitates may be formed where mere coloration or clouding is described as occurring. By means of the table, the origin of any simple tannin infusion is said to be ascertainable, but in the case of mixed infusions the indications are less reliable. In such cases, color-reactions are apt to mislead, and it is safer to rely on the categorical test of precipitate or no precipitate, coloration or no coloration, without regard to the tint.

In some cases, only negative peculiarities are recorded, and the material cannot be positively identified in admixture with other tannin matters giving positive indications with the same reagents. Thus an infusion of myrabolams could not be distinguished with certainty from an infusion of divi-divi, where any other material, such as gambier, was present, which gives a deep coloration with concentrated sulphuric acid.

In addition to the reactions described in the table, the identification of the products of the action of heat on tannins, and of their treatment with dilute acids and fusing caustic alkali, affords a valuable means of differentiation.

Most, if not all, of the ordinary varieties of tannin give with an ammoniacal solution of potassium ferricyanide a deep red coloration, rapidly becoming brownish, especially on addition of excess of the reagent.

The extract from a bark yields more ash than that from a wood.

Reagent.	Myrabolams.	Divi-divi.	Valonia.	Oak-Bark.	Chestnut Wood (Extract).
Boiled with equal volume of dilute sulphuric acid (1 to 9).	Pale deposit (ellagic acid) on cooling.	Pale deposit (ellagic acid) on cooling.	Slight pale deposit.	Slight pale deposit or turbidity on cooling.	No deposit.
Bromine water.	No precipitate.	No precipitate.	No precipitate.	Pale precipitate.	No precipitate.
Dilute ferric chloride.	Blue-black precipitate.	Dark blue precipitate.	Blue - black precipitate.	Bluish-black precipitate.	Blue - black precipitate.
On adding ammonia.	Brown precipitate.	Dark red precipitate.	Red - brown precipitate.	Red - brown precipitate.	Purple precipitate.
Solution tartar emetic.	No precipitate.	Faint clouding.	No precipitate.	No precipitate.	Slight clouding.
Add ammonium chloride.	Light precipitate.	Dense precipitate.	Pale precipitate.	Whitish precipitate.	Pale precipitate.
Copper sulphate.	Faint clouding.	Slight green precipitate.	No precipitate.	Slight precipitate.	No precipitate.
On adding ammonia.	Dense dark precipitate.	Dense dark precipitate.	Dark reddish precipitate.	Brown precipitate.	Light brown precipitate.
Lime-water.	Yellow precipitate turning greenish.	Yellow precipitate turning purple.	Yellow precipitate turning red-purple.	Brown precipitate.	White precipitate turning light blue.
Ammonium molybdate in nitric acid.	Dirty yellow precipitate.	Dark greenish precipitate.	Dark greenish precipitate.	Greenish precipitate.	Yellow color.
With sodium sulphide exposed to air.	Yellow color.	Yellow color.	Turns purplish-red.	Turns red.	No change.
Add concentrated sulphuric acid to one drop of infusion.	Yellow color.	Intense crimson.	Deep yellow.	Deep red precipitate on dilution.	Light yellow.
Lead nitrate.	Light yellow precipitate.	Dark yellow precipitate.	Pale precipitate.	Brown precipitate.	White precipitate.
Cobalt acetate.	Buff precipitate.	Buff pink precipitate.	Dirty pink precipitate.	Brown precipitate.	Flesh - colored precipitate.
Manganese acetate.	Yellow precipitate.	Yellow precipitate.	Dirty yellow precipitate.	Brown precipitate.	White precipitate.
Uranium acetate.	Dark red color.	Dark red color.	Dark red color.	Dark brown precipitate.	Crimson color, turning dark red.
Ammonical picric acid solution.	No precipitate.	No precipitate.	Brown precipitate.	No precipitate.	No precipitate.
Potassium bichromate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.

Hungarian Larch (Extract)	Hemlock (Extract).	Mimosa Bark.	Cutch (Pegu).	Gambier (Cube).	Gallotannic Acid, 1 per cent.
Yellow flocculent deposit separates quickly.	Abundant red flocculent deposit.	Heavy red deposit on cooling,	Light red deposit on cooling.	Reddish deposit on cooling.	Usually some pale deposit.
Yellow precipitate.	Yellow precipitate.	Yellow precipitate:	Yellow precipitate.	Yellow precipitate.	No precipitate.
Dull brown precipitate.	Dirty green precipitate.	Full brown precipitate.	Green-black precipitate.	Intense green color.	Blue-black precipitate.
Dull red precipitate.	Reddened precipitate.	Purple color.	Dark red precipitate.	Reddened.	Reddened precipitate.
No precipitate.	No precipitate.	White precipitate.	No precipitate.	No precipitate.	No precipitate.
Pale precipitate.	Slight pale precipitate.	Dense white precipitate.	Pale precipitate.	Faint clouding.	White precipitate.
Slight cloud.	Pale precipitate.	Slight precipitate.	Dense precipitate.	No precipitate.	No precipitate.
Deep blue coloration.	Dark green coloration.	Deep red precipitate.	Deep violet coloration.	Dark green coloration.	Brown precipitate.
Dirty brown precipitate.	Brown precipitate.	Slight reddish precipitate.	Slight cloud, soluble in excess.	No precipitate.	Pale precipitate turning blue.
Slight clouding.	Slight precipitate.	Brown precipitate.	Slight cloud, soluble in excess.	No precipitate.	Yellow color.
No change.	No change.	Turns red.	Slight reddening.	No change.	No change.
Dark brown or crimson.	Intense crimson.	Intense purple-red.	Deep red. no precipitate on dilution.	Dark brown or crimson.	Yellow.
Pale precipitate.	Pale precipitate.	Clouding.	No precipitate.	Faint clouding.	White precipitate.
Purplish precipitate.	Purple precipitate.	Brown precipitate.	Brown precipitate.	No precipitate.	Purple precipitate.
Slight clouding.	Slight precipitate.	No precipitate.	No precipitate.	No precipitate.	White precipitate.
Slight darkening.	Light brown precipitate.	Dark red color.	Dark red color.	Dark red color.	Crimson color. Brown precipitate.
No precipitate.	Clouding.	No precipitate.	No precipitate.	No precipitate.	No precipitate.
No precipitate.	Brown precipitate slowly formed.	Brown precipitate.	Brown color.	Brown precipitate slowly formed.	Brown precipitate.

The ash of an oak or pine extract contains manganese and has a green color, or becomes green on being fused with sodium carbonate and a little nitre.

On shaking a concentrated solution of quebracho extract with acetic ether, the ethereal layer becomes at first green and then brown.

The bark and extract of the American chestnut oak (*Quercus castanea*) contains a substance exhibiting, like æsculin, a powerful blue fluorescence, especially in alkaline solution.

Pure tannins yield different kinds of derivatives with phenylhydrazine; but as these do not crystallize no satisfactory separation can be made in this manner.

Sumac extracts are distinguished by a peculiar tarry smell, and yield a high ash.

H. R. P r o c t e r (*Jour. Soc. Chem. Ind.*, xiii, 487) gives the following tables for the qualitative recognition of tanning materials:

<div align="center">TABLE I.</div>

Bromine Water produces a precipitate.		Bromine Water produces a precipitate.		Bromine Water produces no precipitate.	
Iron-Alum gives Greenish Blacks.		Iron-Alum gives Blue or Purplish Blacks.		Iron-Alum gives Blue Blacks.	
(Catechol Tannins.)		(Mixed and Doubtful.)		(Pyrogallol Tannins.)	
$CuSO_4$ with excess of NH_4OH.		$NaNO_2$ with 5 drops of $\frac{N}{10}HCl$.		$NaNO_2$ with 5 drops of $\frac{N}{10}HCl$.	
Precipitate redissolves.	Precipitate does not redissolve.	No reaction, or, at most, darkening.	Color change from Red towards Blue or Green.	Color change through Red to Blue.	No reaction.
$1a$	1β	$2a$	2β	$3a$	3β
Table II.	Table III.	Table IV.	Table V.	Table VI.	Table VII.

TABLE II.

Class 1a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO$_4$ + NH$_4$OH.	SnCl$_2$ + HCl.	Deal Shaving and HCl.	Na$_2$SO$_3$.	H$_2$SO$_4$.	Lime Water.
Cutches from Ac. catechu wood.	Green-black.	Pp.	No react. darkens.	Pp. redissolves red-violet color.	No react.	Deep violet-red.	Reddens.	Red-brown color.	Reddish pp. slowly formed.
"Thann leaf" extract (a cutch substitute).	Olive-black pp.	"	"	Pp. redissolves brown color.	"	No react.	No react.	Crimson, dilute pink.	No pp.
"Turwar" bark (Cassia auriculata).	Green-black.	"	"	Pp. redissolves red violet.	"	Trace.	Pink color.	Crimson.	Reddish pp.
"Gambene" extract (a gambier substitute).	Green-black color.	"	"	"	"	No react.	Slight pink color.	Crimson, dilute pink.	"
"Teugah" bark (Ceriops Candolleanna).	"	"	No react. darkens pp.	"	Pink color.	"	Pink color.	Crimson.	Bright red pp.
Bark (Acacia leucophlæa).	"	"	No react.	"	"	Slow violet react.	"	Crimson, dilute pink.	Dull brown pp.
Bark (Soymida febrifuga).	"	"	"	Pp. redissolves red-brown.	"	No react.	"	Crimson.	Red brown.
Cork bark (Quercus suber).	Green-black coloration.	"	Reacts somewhat.	Pp. redissolves brown.	No react.	"	Reddens.	Crimson, dilutes pink.	Reddish brown pp.
Green oak (Ital.) (Quercus Ilex.).	"	"	Reacts faintly, if at all.	"	"	"	"	"	"
Garouille (root bark of Kermes oak) (Quercus Coccifera).	"	"	Reacts?	"	"	"	"	"	"

TABLE II.—*Continued.*

Class 1a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
[1] Quercitron bark (*Quercus Tinctoria*).	Green-black coloration.	Pp.	Reacts somewhat.	Pp. redissolves brown.	Light green.	No react.	Doubtful.	Crimson, dilutes pink.	Reddish brown pp.
Gambier (ext. of leaves of *Nauclea gambir*).	Deep green coloration.	"	No react., darkens.	Pp. redissolves olive-green.	Yellow.	Deep violet-red.	Yellow.	Crimson, dilutes brown.	No pp.
[2] "Pruim bast" (leaves of *Colpoon* or *Osyris compressa*).	Green-black.	"	No react.	Pp. redissolves green.	No react.	Pink.	"	"	Light yellow pp.
[3] "Koko." Natal (leaves of *Celastrus buxifolia*).	"	"	"	"	"	No react.	"	Dark brown.	Bright yellow pp.
Larch bark (*Larix Europæa*).	Green-black coloration.	"	No react., darkens.	Pp. redissolves olive-green.	Pink coloration.	"	No react., darkens.	Deep red-brown.	Rusty pp.
Hemlock bark (*Tsuga* or *Abies Canadensis*).	Olive-green reddish pp.	"	No react., pink with NaNO₂.	Pp. redissolves neutral tint.	"	"	Reddens.	Crimson, dilutes pinkish.	Red-brown pp.
"Larch" extract from (*Abies excelsa*).[4]	Green-black or brown.	"	No react.	Pp. redissolves olive-green.	"	"	Darkens.	Deep red-brown.	Brown pp.

[1] Dyes yellow with Al and Sn mordants.

[2] Used at Cape of Good Hope as sumac.

[3] Used in Natal as sumac substitute.

[4] *Fichte, Rothtanne,* Norway or common spruce. *Abies pectinata* the *Weiss* or *Edel-Tanne* or silver fir, is said to give a blue-black with iron.

TABLE III.

Class 1β.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
Willow bark (Russian. Sp. unknown).	Green-black.	Pp.	No react.	Dense pp.	No react.	Violet faint.	Pink coloration.	Red-brown not intense.	Slight greyish pp.
Acacia Angica or Piptadenia macrocarpa.	"	"	"	Dense chocolate pp.	Pink or violet color	"	Reddens somewhat.	Crimson dilutes pink.	Reddish pp.
Acacia catechu bark.	"	"	"	Dense violet-black pp.	Possible trace.	Trace.	Pink color.	Red-brown.	Flesh color pp.
"Thorn tree" bark (Acacia horrida) (Cape).	"	"	No react, darkens.	Dense pp.	No react.	Doubtful.	"	Dull crimson not intense.	No pp.
Mangrove bark extract (Rhizophora mangle).	"	"	No react.	Reddish-black.	Slight reddening.	No react.	Slight reddening.	Red-brown.	Red pp, darkened by excess.
Quebracho wood extract (Quebracho or Loxopterygium Lorenzii).	Green-black coloration.	"	"	Dense pp.	Pink color pp.	Trace.	Doubtful.	Crimson coloration dilutes pink.	Light brown pp.
"sugar bush" bark (Cape) (Protea mellifera).	Green-black.	"	No react, darkens.	"	No react.	"	"	Red.	Yellow-brown pp.
"Waagenboom" (Cape) (Protea grandiflora).	"	"	"	"	"	"	Pink color.	Crimson dilutes pink.	Light yellow pp.
"Kruppelboom" (Cape) (Leucospermum conocarpam).	"	"	"	"	"	Violet distinct.	"	"	Slight greyish pp.
"Silver tree" (Cape) (Leucodendron argenteum).	"	"	"	"	"	No react.	Pink coloration.	"	Flesh color pp.
¹ Chestnut Oak (Quercus Castanea).	Olive-green coloration.	"	Reacts distinctly.	Decided pp. Insoluble in excess.	"	"	Reddens.	Crimson dilutes pinkish.	Reddish brown pp.

¹ Infusions fluoresce, especially with ammonia.

TABLE IV.

Class 2a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
"Skens," Cypress Sumac (possibly *Coriaria myrtifolia*).	Blue-black pp.	Pp.	No react.	Dark pp.	No react.	No react.	Yellow.	Yellow-brown.	Yellow pp. darkening.
Kliphaut bark[1] (*Rhus Thunbergii*).	Blue-black	"	"	Dense dark pp.	"	"	Pink.	Dull crimson dilutes orange.	Pinkish pp.
Canaigre (Root of *Rumex hymenosepalus*).	Blue-black pp.	"	"	Dense dark pp.	No react. clouds.	Trace violet.	Slight darkening.	Yellow. brown.	Pink coloration greyish pp.
"Talwaan" or "Elandsbontjes" (Root. *Elephantorrhiza Burchellii*).	"	"	No react. Darkens.	"	No react.	"	Pink.	Red.	Reddish-brown pp.
Mimosa or Wattle barks (Various Austral. *Acacia*).	Dirty violet pp.	"	No react.	Dense purple-brown pp.	Slight reddening.	Sometimes trace.	Reddens.	Crimson dilutes pink.	Reddish or yellow-brown pp.
Babool bark. India (*Acacia Arabica*).	"	"	"	Dense dark pp.	Some trace	Faint trace	Slight darkening.	Crimson dilutes orange.	Dark reddish-brown pp.
Dark red Austr. bark (Probably an *acacia*).	"	Pp. needle crystals.	"	Deep violet pp.	No react.	"	Orange-pink.	Crimson dilutes pink.	Bright violet pp.
"White bark" *Algaroba blanca*. South America (*A. prosopis* or *acacia*).	"	Pp.	"	Reddish-black pp.	"	Violet.	Reddens strongly.	"	Red pp. turning violet.

[1] Used at Cape of Good Hope.

TABLE V.

Class 2/3.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO$_4$ + NH$_4$OH.	SnCl$_2$ + HCl.	Deal Shaving and HCl.	Na$_2$SO$_3$.	H$_2$SO$_4$.	Lime Water.
English Oak (*Quercus Robur*).	Blue-black (green with excess).	Pp.	Reacts somewhat.	Slight pp. Dark brown pp.	No react.	Faint react.	Reddens.	Crimson dilutes pink.	Reddish-brown pp.
Jaft or Dchit.[1] Supposed oak product.[2]	Blue-black pp.	"	Reacts red-blue.	Brown pp. Dark brown pp.	No react. Dark brown pp.	"	Some darkening.	"	"

[1] A Persian product, dark scales very rich in tannin (about 40 per cent.).
[2] Strong infusions, dry whitish and iridescent.

TABLE VI.

Class 3a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO$_4$ + NH$_4$OH.	SnCl$_2$ + HCl.	Deal Shaving and HCl.	Na$_2$SO$_3$.	H$_2$SO$_4$	Lime Water.
Aleppo galls (of *Quercus infectoria*).	Blue-black pp.	No pp. slight scum.	Reacts red to blue.	Dark pp. insoluble.	Light yellow pp.	No react.	No react.	Greenish to dirty Yellow.	Pale pp. turning bluish-green.
Sumac (leaf of *Rhus coriaria*).[1]	"	No pp.	Reacts feebly.	Dark-brown insoluble pp.	No react.	"	"	Yellow.	Yellow pp. turning bright green.
Myrabolams (*Terminalia chebula*).[1]	"	"	Reacts red to blue.	Dark insoluble pp.	"	"	Yellow.	"	Yellow pp. turning greenish.

[1] Dyes yellow on Sn mordants.

TABLE VI.—*Continued.*

Class 3a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
Pomegranate rind (*Punica granatum*).	Blue-black pp.	No pp.	Reacts red to blue.	Dark-brown insol. pp.	No react.	No react.	No react.	Orange-brown.	Bright yellow pp. turning red with excess.
Algarobilla (*Cæsalpinia brevifolia*).	"	"	"	Dense dark pp.	"	"	Deep yellow.	Deep yellow-brown.	Bright yellow pp. darkens some.
[1] Divi-divi (*Cæsalpinia coriaria*).	"	"	"	"	"	"	No react.	Crimson.	Yellow pp. turning red-purple.
Algarobo (*Prosopis dulcis*).	"	"	Red to olive.	"	"	"	Yellow.	Yellow to olive.	Yellow pp. turning black.
Valonia (*Quercus Aegilops*).	"	"	Red to blue.	Dark, reddish pp.	"	"	Purplish-pink.	Deep yellow.	Yellow pp. turning red-purple.
[2] "Oakwood" extract (oak or chestnut).	"	"	"	Purple-brown pp.	"	"	Reddens.	Yellow-brown.	"

[1] Moderately strong potassium nitrite solution precipitates divi, but not *dilute* oak-wood solutions; pp. soluble in hot or *much* cold water.

[2] *Crude* chestnut wood extract may be distinguished from oakwood by its violet reaction with ammonium sulphide. (*Gerber*, No. 261, p. 157.)

TABLE VII.

Class 3β.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
Pure gallotannic acid.	Blue-black pp.	No pp.	No react.	Dark pp.	No react.	No react.	No react.	Yellow.	Pale pp. turning blue.
Babool pods (Acacia Arabica).	Blue-black.	"	No react, darkens.	Dark green color.	"	Faint violet.	"	Reddish violet.	Pink color. No pp.

TABLE VIII.

Class 3β.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shaving and HCl.	Na₂SO₃.	H₂SO₄.	Lime Water.
Catechol.	Dark green color.	No pp.	Turns yellow.	Green color.	No react.	No react.	"	Green color.	No react.
Protocatechuic acid.	"	"	Turns brown.	No pp.	"	"	"	No react.	"
Phloroglucol.	No react.	Bulky white pp.	Turns olive-green.	"	"	Red violet color.	"	Slight yellow.	"
Pyrogallol.	Blue-black turning green and brown.	No pp.	Turns yellow.	Brown color.	"	No react.	"	Brown color.	Violet rapidly turning brown.
Gallic acid	Blue-black color.	"	Turns brown.	"	"	"	"	No react.	White pp. rapidly turning blue.

TABLE IX.

REACTIONS OF PURIFIED OAK BARK TANNINS. (TRIMBLE, *Tannins*, VOL. II., P. 88.)

	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO₄ + NH₄OH.	SnCl₂ + HCl.	Deal Shavings and HCl.	Na₂SO₃.	Lime Water.
Black oak (*Q. tinctoria*)	Green color and pp.	Yellow pp.	Brownish-yellow pp.	Pp. Green color.	Yellow with some pink.	Violet color.	Yellow color.	Pp. turning pink then red
Pin oak (*Q. palustris*)	"	"	Pinkish color changing to brown pp.	Pp. Brownish-green color.	Pink color.	"	Pink color.	"
Scarlet oak (*Q. coccinea*)	Bluish-green color. Green pp.	"	Brown pp.	Pp. Green color.	Pinkish color.	"	Pinkish yellow color.	Pp. turning reddish.
Spanish oak (*Q. falcata*)	Green color and pp.	"	"	Pp. Red-brown color.	Yellow color some pink.	"	Yellow with pink streaks.	"
White oak (*Q. alba*)	"	"	"	Pp. Brown-green color.	Pinkish color.	"	Pinkish color.	Pp. turning pink.
Willow oak (*Q. phellos*)	"	"	"	Pp. Red-brown color.	Very yellow color.	"	Yellow with pink streaks.	Pp. turning green, liquid reddish.
Chestnut oak (*Q. prinus*)		"		No pp. Greenish-brown color.				Pp. turning pink.
Swamp white oak (*Q. bicolor*)		"						"
English oak (*Q. robur*)	Bluish-green color. Green pp.	"	Pink color changing to brown pp.	Pp. Red-brown color.	Decided pink color.	Violet color.	Pink color.	"
Indian oak (*Q. semicarpifolia*)	Green color and pp.	"	Brownish-yellow pp.		Pink color.	"	Yellow color.	"

The reagents used in the above tests are prepared and employed as follows:

Ferric alum, a one per cent. solution. This salt appears to be better than ferric chloride or acetate. It may be reasonably assumed that any tannin which gives a distinctly greenish black with iron is a catechol derivative, but there are a large number of materials, especially among the acacias or mimosas, which give purplish blacks, but are almost certainly catechol tannins ; and on the other hand the oak barks which Trimble has proved to be catechol tannins, and most of which give green blacks with iron, also yield bloom or ellagic acid, and are therefore also allied to gallic acid. Another reagent is therefore employed in the preliminary classification, viz.,

Bromine water: it is best to add this drop by drop to 2 to 3 c.c. of the infusion in a test-tube until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline and on this account less conspicuous, but it is usually a distinct yellow or brown flocculent one. In general terms it may be said to be a reagent for the catechol tannins; precipitating all which give green blacks with iron, and many which give blue or violet-blacks, which are reasonably suspected of containing catechol. It does not precipitate any recognized pyrogallol tannin, but several which yield ellagic acid (bloom), such as oak barks.

Nitrous Acid Reaction.—This reaction, which is believed to be a new one, is obtained by adding to a few c.c. of the very dilute infusion in a porcelain basin a distinct excess of freshly prepared solution or a few crystals of sodium or potassium nitrite, and then 3—5 drops of decinormal sulphuric or hydrochloric acid. In typical cases the solution instantly turns pink or crimson, and slowly changes through purple to a deep indigo-blue; but in others, as sumac, where the reaction is feeble, and masked by other changes, the final color is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown coloration or precipitate, but "reaction" in the tables invariably means a series of color-changes as above described. The reaction is given by all tanning materials which yield ellagic acid or "bloom," but not by ellagic acid itself, nor by pure gallo-tannic acid. It is therefore probably a reaction of ellagitannic acid, and is valuable for subdividing the mixed and pyrogallol tannins. It may also be obtained faintly from some of the oaks in Class 1 β.

Copper sulphate and ammonia. A one per cent. solution of copper sulphate is employed, and is added to the tannin solution first, followed by ammonia in slight excess.

Stannous Chloride and Hydrochloric Acid.—This reagent consists of a strong solution of stannous chloride in concentrated hydrochloric acid. If about 10 c.c. of this are added to 1 c.c. of the tanning material infusion, in a porcelain basin, and allowed to stand for 10 minutes, coniferous tans, mimosas, and some others give a very marked pink coloration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the coloration appears very strongly.

Deal Shaving and Hydrochloric Acid.—A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier, and a few other materials, and of solution of phloroglucol itself, the spot becomes at once a bright red or violet, but in many cases the reaction is faint, and only appears after some hours. It probably always indicates the presence of phloroglucol. The statement that catechol gives a similar reaction appears to be an error.

Sodium Sulphite.—A few drops of the tannin solution are placed in contact with a crystal of sulphite on a tile. Many tanning materials produce red or pink colorations, but in no case so marked a reaction as valonia.

Sulphuric Acid.—About 1 c.c. of concentrated acid is cautiously added to a few drops of the tannin solution in a test-tube so the acid forms a layer underneath the tannin. The ring of color at the junction of the two liquids is noted, and then they are mixed by shaking and diluted with water.

Lime Water is a most useful reagent. The reaction is best seen in a shallow porcelain dish, and time must be allowed for the changes to take place.

The Infusions of tanning materials employed should contain about 0.6 gm. of dry soluble matter in 100 c.c.

Most tannins possess dyeing properties, giving a variety of brownish or yellowish shades on textiles. These coloring principles have not been much examined, but there seems to be an intimate connection between the coloring principle and the tannin matters contained in the same plants. On decomposition, the same acid, and in some cases the same phenol, is obtained from both. The following table will show the correspondence in the

decomposition products of the tannin and its respective coloring matter:

	Tannin.	Decomposition product of tannin.	Coloring Matter.	Decomposition product of coloring matter.
Quebracho Colorado.	Quebracho-tannic acid.	Phloroglucinol and Protocatechuic acid.	Fisetin.	Resorcinol and Protocatechuic acid.
Rhus Coriaria. Rhus Cotinus.	Gallotannic acid.	Gallic acid.	Myricetin.	Phloroglucinol and Gallic acid.
Gambier Catechu. Acacia Catechu.	Catechin.	Phloroglucinol and Protocatechuic acid.	Quercetin.	Phloroglucinol and Protocatechuic acid.
Divi-divi.	Ellagitannic acid.	——	Ellagic acid.	——

A. G. Perkin (J. C. S., 1897, 170), finds that the coloring principle of Cape sumac is a glucoside o s y r i t r i n, $C_{27}H_{30}O_{17} + 2H_2O$, which is decomposed by acid into quercetin and glucose. Venetian sumac showed the presence of myricetin and not quercetin as given by Löwe (Zeit. Anal. Chem., 1874, 127).

Valonia, divi-divi, myrabolams, algarobilla, and gall-nuts, owe their dyeing powers to ellagic acid, and contain no member of the quercetin group.

Analytical Methods for Determining Tannic Acids and Tannins.

A great number of methods have been described for determining tannin and assaying tannin-yielding materials. In many instances the authors have ignored the fact that gallic acid, while reacting in many respects like tannin, does not form stable insoluble compounds with gelatin and albumin, and hence is valueless for the purpose of tanning.[1]

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[1] A little consideration of the subject will show that a general method of determining the tannin in all kinds of tannin matters is not likely to be devised. The problem is comparable to that of devising a general and simple method of determining the metals forming colored salts—say copper, iron, chromium, cobalt, and

SAMPLING OF TANNIN MATERIALS is often a troublesome operation, and together with the difficulty attending complete extraction is a fertile source of error.

When available, a steel mill is the best means of roughly pulverizing most tannin materials. With the exception of barks, the grinding can be effected by a disintegrator with fine screens, taking great care to prevent the escape of dust. Barks may be sampled by cutting each fragment with a small circular saw or rasp driven by a lathe, and collecting the dust.

In the absence of the foregoing appliances, bark and valonia may be cut with strong shears, and myrabolams broken roughly with a hammer. In sampling valonia care must be taken to get a due proportion of the beard, and in taking myrabolams it must be remembered that the bad berries are light and work towards the top of the bag. The sample being partially reduced by one of the above means, the moisture (usually 15 to 16 per cent.) must be determined by drying at 100° C., and the thoroughly dried sample further ground by passing it through a coffee-mill. The ground sample must be again dried before weighing for analysis, as it is very hygroscopic.[1]

nickel—in presence of zinc, aluminium, and lead, the salts of which are usually colorless. It is easy to separate copper from zinc, iron from aluminum, and nickel from lead, but there is no method which will separate copper, iron, and nickel at one operation from zinc, aluminum, and lead. If, in addition, it were extremely difficult to obtain some of these metals in a state of purity, and they were liable to change by the action of reagents, the problem would be rendered still more difficult. Yet this fairly represents the position of the chemistry of the tannins.

[1] The International Association of Leather-Trades Chemists, in its standard methods of Tannin Analysis, recommend the following precautions in drawing samples:

(a) *Liquid Extracts.*—"In drawing samples, at least 5 per cent. of the casks must be taken; the numbers being selected as far apart as possible. The heads must be removed and the contents mixed thoroughly by means of a suitable plunger, care being taken that any sediment adhering to sides or bottom should be thoroughly stirred. All samples must be drawn in the presence of a responsible person."

(b) "Gambier and pasty extracts should be sampled from not less than 5 per cent. of blocks, by a tubular sampling tool, which shall be passed completely through the block in *seven* places. Solid extracts shall be broken, and a sufficient number of portions drawn both from the 'inner' and 'outer' parts of the blocks to fairly represent the bulk. In both cases, samples shall be rapidly mixed and enclosed at once in an air-tight bottle or box, sealed and labelled."

(c, d, e) "Valonia, algarobilla, and all other tannin materials containing dust or fibre shall be sampled, if possible, by spreading at least 5 per cent. of the

THE EXTRACTION OF TANNIN-MATTERS is better effected by treating the sample at once with a large quantity of water than by repeated treatment with smaller quantities.   10 grammes weight of valonia or myrabolams, 20 of oak-bark, or a corresponding weight of other tannin material is placed in a flask of at least $1\frac{1}{2}$ litres capacity and covered with 1 litre of cold distilled water. This is raised to ebullition (great care being necessary at the moment of boiling to prevent frothing up and boiling over), and the liquid is kept boiling briskly for half an hour, a funnel being placed in the mouth of the flask.   The liquid is then allowed to cool, rinsed with the solid residue into a litre flask, which is filled with cold water to the mark, and the solution well shaken and filtered.   If the solution is obstinately turbid it may be clarified by agitation with kaolin, followed by re-filtration.   With tannin-matters which are apt to deposit ellagic acid or red anhydrides (phlobaphenes), higher results are obtained if the solution is cooled rapidly and filtered at once than if it is allowed to stand for twenty-four hours.   Hence, in this respect, a uniform practice is desirable.[1]   If the titration is not to be performed at once, 0.5 c.c.

bags in layers, one upon another, on a smooth floor, and taking several samples vertically to the floor.   Where this cannot be done, the sample must be drawn from the centres of a sufficient number of bags.   While valonia and most tannin materials may be sent to the chemist ground, it is preferable that divi-divi and algarobilla shall be unground.   Bark in long rind, and other materials in bundles, shall be sampled by cutting a short section from the middle of 3 per cent. of the bundles with a saw or other sharp tool.''

(f) Barks and other solid tannin materials.   '' The whole sample, or not less than 250 gr., shall be ground in a mill until it will pass through a sieve of 5 wires per centimetre.   When materials, such as barks and divi-divi contain fibrous material which cannot be ground to powder, the ground sample shall be sieved and the respective parts which do and do not pass through the sieve shall be weighed separately, and the sample for analysis shall be weighed so as to contain like proportions.''

[1] The strength of tannin solution employed shall be such that from evaporation of 100 c.c., the residue shall amount to between 0.6 and 0.8 gr.

Solution of Liquid Extracts.—A sufficient quantity shall be weighed into a cov-ered basin or beaker, from which it shall be washed into a litre flask with about 500 c.c. of boiling water, well shaken and the flask filled nearly to the mark with cold water.   The neck being covered with a small beaker, it shall be placed under a cold-water tap, or otherwise rapidly cooled to a temperature between 15° and 20° C., and made up to the mark, after which it shall be thoroughly mixed, and the filtration at once proceeded with.

The filtration shall take place through Schleicher and Schuell's filter paper, No. 602.   The first 150 or 200 cc. of the filtrate shall be rejected, or employed for the determination of the non-tannins.   Where a clear filtrate cannot be ob-

of glacial acetic acid should be added to check oxidation. In dissolving *extracts*, it is desirable to pour them into water actually boiling, as many become permanently insoluble if first mixed with water at too low a temperature.

Tannin solutions free from coloring matters may be prepared by adding zinc sulphate and ammonium sulphate to the solution; tannate of zinc is thus precipitated, which is washed with ammoniacal water. It is then suspended in five times its volume of water and decomposed by dilute sulphuric acid. A solution of barium sulphide is added till no further precipitate is formed. The precipitate, which consists of zinc sulphide and barium sulphate, is removed, and an almost colorless solution of tannin remains. This method is applied to the manufacture of *stainless extracts*.

Tan liquors may be decolorized by treating with lead nitrate, and afterwards adding alum and borax. Strontium hydrate and carbonate are also used for the precipitation of the coloring matters; sulphuric acid being added to the filtrate to remove the excess of strontium salt. Clarification is also accomplished by electrolyzing the liquid to which has been added oxalic acid and sodium chloride. Sumac may be decolorized with good results by the use of ox-blood.

Of the numerous methods which have been devised for the assay of tannin-matters, nearly all those worthy of detailed description are based on the principle of precipitation of the tannin by a solution of gelatin or its absorption by a gelatinous substance. In some cases the weight of the precipitate formed, or the increase in the weight of the solid gelatinous substances has been ascertained, but a preferable plan is to ascertain the quantity of tannin precipitate by comparing the liquid after the treatment with the original

tained, the use of a little kaolin, previously washed with a portion of the tannin solution, is permissible.

Solid extracts shall be dissolved by stirring in a beaker with boiling water, the undissolved portions being allowed to settle, and treated with further quantities of boiling water, and the solutions poured into a litre flask. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Extraction of Solid Materials.—Such quantities shall be weighed as will give an infusion of the strength already prescribed. Not less than 500 c.c. of the infusion shall be extracted at a temperature not exceeding 50° C., after which the temperature shall be raised to 100° C., and the extraction continued till the percolate is free from tannin and the whole made to one litre, the weaker portions of the solution being concentrated if necessary by evaporation in a flask, in the neck of which a funnel is placed.—(*Int. Assoc. Leath. Trades Chemists.*)

untreated solution. This is done by Hammer by taking the specific gravity; by Simand and Weiss by weighing the solid matter left on evaporation; and by Löwenthal by determining the volume of standard permanganate solution decolorized by the solution before and after removal of the tannin. These methods, which appear simple enough it principle, are in practice surrounded with very considerable difficulties, especially when considerable quantities of gallic acid are present.

THE OXIDATION-METHOD OF TANNIN ASSAY.

This process, which was first worked out by L ö w e n t h a l, is based on the fact that tannin is oxidized in acid solutions by permanganate, though the slowness of the oxidation and the want of definition of the end-reaction render the method unsuitable without modification. By addition of a considerable quantity of indigo the oxidation of the tannin is controlled, and the end-reaction is rendered perfectly definite. As solutions of commercial tannin-matters contain other oxidizable matters besides tannins, it is necessary to separate these and titrate a second time, in order to ascertain the volume of permanganate actually required by the tannin present. This separation may be effected by digestion with hide-raspings, or more conveniently by a solution of gelatin, the use of which was first suggested by Estcourt.

In practice, Löwenthal employs a mixed solution of gelatin and common salt, to which a small quantity of sulphuric or hydrochloric acid is added. In using this form of the process it is generally necessary to let the mixture stand several hours in order to obtain a clear filtrate, besides which the gelatin remaining in solution (or its associated impurity) has a slight though generally negligible reducing action on the permanganate. In some cases, even after long standing, filtration is very tedious, and it has also been proved by F. S i m a n d (*Jour. Chem. Soc.*, xliii. 1237), that a certain proportion of the tanno-gelatin precipitate, varying with the acid and kind of tannin present, remains in solution, and hence that the results obtained by the process are below the truth.

On account of the objections to Löwenthal's process as commonly conducted, H. R. P r o c t e r has proposed a modification of it (*Jour. Soc. Chem. Ind.*, iii. 82), in which the excess of gelatin is removed by saturating the liquid with common salt, and the filtration is facilitated by addition of kaolin. A perfectly clear filtrate wholly free from tannin, and nearly so from gelatin, is thus obtained without difficulty. The following are the details of the process:—

a. 10 grammes of a sample of sumac or valonia, or 20 grammes of finely-ground bark, are exhausted by boiling with water in the manner described on page 18, and the infusion allowed to cool and diluted to 1 litre. 5 c.c. measure of this solution is run into a porcelain basin and diluted to 750 c.c. by addition of distilled or good drinking water, and 20 c.c. added of an indigo solution, a litre of which contains 5 grammes of the purest indigo-carmine,[1] and 50 c.c. of concentrated sulphuric acid. A solution containing 1 gramme of potassium permanganate per litre is then dropped in very slowly with vigorous stirring, until the liquid becomes transparent, when the addition is continued more cautiously, with occasional pauses, until the clear yellow liquid appears of a faint pink color on the margin. The titration is repeated, the measures of permanganate required in the two cases being added together and called *a*.

In employing the oxidation-process, it is essential that the volume of permanganate required by the tannin should *in no case* exceed two-thirds of that reduced by the indigo. If the result of the titration shows that this proportion has been exceeded, the experiments must be repeated with a smaller quantity of the tannin solution.

b. 50 c.c. of the tannin solution should be mixed in a flask with 28.6 c.c. of a freshly made and filtered solution of gelatin[2] (2 grm. per 100 c.c.). After shaking, the liquid is saturated with common salt,[3] which increases the volume to 90 c.c. 10 c.c. of dilute

[1] The indigo-carmine (sodium sulphindigotate) must be of such quality that the solution when oxidized by permanganate is a pure yellow color, free from a trace of brown or orange. Any contamination with indigo-purple, which gives brown oxidation-products, is quite fatal to the accuracy of the analysis. The indigo solution should be of such strength that 20 c.c., diluted to 750 c.c. with water, shall require from 14 to 16 c.c. of standard permanganate for its oxidation.

[2] 2 grammes weight of good gelatin is allowed to swell in distilled water for a few hours, then melted by immersing the flask in boiling water, and the resultant solution made up to 100 c.c.

[3] B. H u n t (*Jour. Soc. Chem. Ind.*, iv. 263) has shown that the excessive quantity of salt recommended by Procter causes the precipitation of a notable quantity of gallic acid when much is present. Hence, he prefers to mix 50 c.c. of the tannin solution with 25 c.c. of a 2 per cent. solution of gelatin, and then add 25 c.c. of a saturated solution of common salt containing 50 c.c. of strong sulphuric acid per litre. Kaolin is next added, and the mixture well agitated and filtered, and in all other respects Procter's method of operating is adhered to. Hunt's modification is approximately a return to Löwenthal's original method, and introduces its attendant error. Hence Hunt's mode of working is only to be recommended in presence of much gallic acid.

sulphuric acid (containing one volume of the concentrated acid in 10) should next be added, and then about 10 grammes of pure kaolin or barium sulphate. The flask should now be vigorously shaken for a few minutes, and the liquid passed through a dry filter. This is effected rapidly, and the filtrate is perfectly clear. Two quantities of the filtrate of 10 c.c. each ($= 5$ c.c. of original infusion) are then treated with indigo solution, and titrated with standard permanganate as before, the result being called b. The difference $(a-b)$ between the measure of permanganate employed for the two quantities of unprecipitated tannin infusion (a), and that decolorized by the two portions of the filtrate, gives the volume of permanganate solution decolorized by the tannin in 10 c.c. of the original infusion.[1]

c. 10 c.c. of a decinormal solution of oxalic acid (6.3 grammes of crystallized oxalic acid, $C_2H_2O_4 + 2H_2O$, per litre) are diluted with distilled water to about 500 c.c., warmed to about 60° C., 20 c.c. of pure dilute sulphuric acid added, and standard permanganate run in with constant stirring till a pink coloration, remaining permanent for a minute, shows that oxidation is complete. The volume of permanganate consumed, which is called c, is evidently that required for the oxidation of 63 milligrammes of crystallized oxalic acid.

The proportion $c : (a-b) = 63 : x$ will give the number of milligrammes of oxalic acid corresponding in reducing power to the tannin in 10 c.c. of the infusion assayed. If 10 grammes of the sample were extracted and the solution made up to 1 litre, 10 c.c. of the infusion represented 0.1 gramme of the tanning material, and hence the number of milligrammes of oxalic acid will be *the percentage of tannin expressed in terms of crystallized oxalic acid.* It is frequently convenient to express the results of the assay in this way, since what is required in practice is not the absolute weight of tannin in the various materials, but their *comparative* richness in tannin. It would of course be of interest to express the results of tannin assays in actual percentages of tannin, but unfortunately the different varieties of tannic acid have different reducing powers, and the expression of the results of the assay of oak-bark or cutch in terms of gallotannic acid would be more objectionable than the expression of assays of all kinds of tannin-matters in

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. [1] F. Gantter (*Zeits. f. angew. Chem.*, 1889, 577) recommends that the oxidation with potassium permanganate be carried out in a hot instead of a cold tannin solution, without the presence of a special indicator.

terms of oxalic acid.[1] The actual reduction-equivalents of the different kinds of tannin are very imperfectly known. N e u b a u e r states that of g a l l - t a n n i n at 41.57; that is, 41.57 grammes of gall-tannin possess the same reducing power on permanganate that is possessed by 63 grammes of crystallized oxalic acid ($C_2H_2O_4$. $2H_2O$), or 56 grammes of iron in the ferrous state. This is tantamount to the statement that 41.57 grammes of gall-tannin decolorize a volume of permanganate solution yielding 8 grammes of available oxygen. Neubauer's equivalent for gallotannic acid has been confirmed by I s h i k a w a (*Chem. News*, xlii. 274), who found 41.688 as the figure for the tannin of *Kibushi*, or Japanese gallnuts. C o u n c l e r and v o n S c h r o e d e r, on the other hand, find the equivalent to be only 34.25.[2] For o a k - b a r k t a n n i n, N e u b a u e r gives the equivalent 62.36, which is confirmed by O s e r ' s figure, 62.35, and approximately by that of Simand, 61.1. The reduction-equivalents of other varieties of tannin are almost wholly unknown.[3] Oser's and Neubauer's figures for oak-bark tannin show a reducing power nearly identical with that of oxalic

[1] V o n S c h r o e d e r has suggested the use as a standard of commercial gallotannic acid, the moisture in which has been determined by drying at 95° C., and which has been proved to contain not more than 5 per cent. of non-tannin matters unprecipitable by hide or gelatin ; dividing the result obtained by 1.05 to allow for the slightly higher reducing power of the impure tannin. Procter has proposed to employ gallic acid for standardizing the permanganate, as it is readily obtained pure, and is oxidized in presence of indigo in a manner very similar to gallotannic acid.

[2] This discrepancy has been shown by von Schroeder to be due to the different manner in which the permanganate was added in the titration, Neubauer employing the "drop method," while Councler and von Schroeder added the solution in successive quantities of 1 c.c. with a short interval between each addition. This modification seriously effects the volume of the standard solution consumed (see page 80).

[3] The figures recorded by G ü n t h e r are so remarkably at variance with those of the observers quoted in the text, that there is probably some undiscovered error. His results were:—gallotannic acid, 16.25; sumac tannin, 16.5; caffetannic acid, 17.0; oak-bark tannin, 16.0; kinotannic acid, 14.0; ratanhia-tannin, 17 to 18.5, and tormentilla-tannin, 17.5. He also gave some figures for mimotannic acid and catechin, which when corrected for an error of calculation are 2.77 and 2.66 respectively. Lehmann, in checking these experiments, found the equivalent 2.57 for mimotannic acid and 2.42 for catechin. There is evidently something grossly wrong here, for it would result in a sample of cutch which showed 63 per cent. of tannin expressed in terms of oxalic acid being stated to contain only 2.67 per cent. of catechu-tannic acid, though a far larger proportion than that could be actually prepared from it.

acid ($= 63$), and hence, in the present state of the subject, the results of the titration may be conveniently expressed in terms of oxalic acid.   An alternative plan is to state the strength of the tannin-matter in terms of "oxygen consumed."   Each 1 c.c. of a solution of potassium permanganate (containing 1 gramme of the salt per litre) which may have been decolorized by the tannin, represents 0.000253 of "oxygen consumed," or 0.00199 (practically 0.002) gramme of crystallized oxalic acid.   Neubauer's equivalent for gall-tannin is practically two-thirds of the bark and oxalic acid figures.   The first figure is applicable to galls, and probably to divi-divi, sumac and myrabolams; the second to oak-barks, and probably to oak-wood, valonia, chestnut extract, etc.   Gallic acid consumes a greater volume of permanganate than the tannin from which it is derived.   Hence, as commercial tannin is often largely contaminated with gallic acid, it not unfrequently shows over 100 per cent. of tannin when assayed.[1]

According to C e c h (*Zeitschr. Anal. Chem.*, vii. 134), no interference in the estimation of tannin by permanganate is produced by the presence of acetic acid, citric acid, tartaric acid, malic acid, cane-sugar, dextrin, gum, fat, caffein, or urea, provided the solution be properly diluted.

It cannot be too clearly understood that the permanganate and all other processes for the assay of tannin-matters are merely comparative, and give results worthy of acceptance only when they are used for comparing the qualities of samples of material of the same character.   Thus, bark may be compared with bark, valonia with valonia, and cutch with cutch, but *all cross comparisons are misleading;* and would be so even if the exact percentage of tannin could be calculated, since the practical and commercial value of tannin materials does not depend on the quantity of tannin only, but on the color and quality of the leather, though the same process should give absolute results of at least approximate accuracy when applied to different materials containing the same variety of tannin.

P. S i s l e y (*Bull. Soc. Chim.* [3], ix, 755) precipitates the tannin as a zinc salt, and oxidizes the latter with permanganate.   Ammoniacal zinc acetate is used for the precipitation, and is made by dissolving 40 grammes zinc oxide in hot, dilute acetic acid (65 c.c.

[1] Mixtures of tannins with gallic acid cannot be valued by the volumetric process, for 1 gram of the dry acid reacts with the same quantity of permanganate as 1.505 gram of dry tannin.   (Heinemann, *Zeits. angev. Chem.*, 1899, p. 245.)

glacial acid and 50 c.c. water), and adding excess of ammonia.
The tannin solution is treated with the zinc solution, and the pre-
cipitated zinc compound rapidly filtered and washed with ammo-
nia water, by which means the gallic acid and other impurities are
removed.   The precipitate is then washed into a suitable vessel,
and titrated with potassium permanganate.

The following figures by Procter show the results to be expected
when applying the permanganate process to the assay of various
tannin-matters.   The determinations were made by the method
already described.

	In terms of Oxalic Acid.	
	Tannin.	Other oxidizable bodies.
Valonia; good Smyrna, ...	29.1 per cent.	2.3 per cent.
" "	30.7 "	2.1 "
" "	30.5 "	1.9 "
" "	32.6 "	2.7 "
Hungarian larch extract, ...	14.78 "	1.95 "
" " "	18.08 "	2.33 "
Chestnut-wood extract (sp. gr. 1.205),	25.53 "	3.68 "
Pegu cutch, ...	63.59 "	2.45 "
Spent liquor,[1]	0.12 "	11.0 "

The permanganate process has been applied by A. Hill to the
determination of tannin in *tea* (*Analyst*, vi. 95).   The average pro-
portion of tannin, in terms of oxalic acid, found in the thirty-two
samples of tea examined was 14.8 per cent., the extreme results
being 6.18 in black Assam tea and 26.90 in a black caper tea.
Other determinations of the proportion of tannin in tea have been
made by O. Kellner (*Jour. Chem. Soc.* lii. 73) and J. F. Geis-
ler (*Analyst*, ix. 220).

The following figures are due to B. Hunt (*Jour. Soc. Chem.
Ind.*, iv. 264).   They show the insoluble matter and total extract

[1] The results of the assay of the spent liquor are instructive.   The liquor origi-
nally contained from 10 to 15 per cent. of the tannins from oak-bark, valonia,
myrabolams, gambier, hemlock, &c., which contact with hide had reduced to the
small proportion of 0.12 per cent.   That a portion had not been absorbed but de-
composed is shown by the large accumulation of oxidizable impurities (equal to
11 per cent. of oxalic acid).   Spent liquors are very pale in color. as also are the
filtrates from the gelatin precipitation, a fact that proves that the coloring matters
present in tannin materials resemble tannin in their behavior to hide and gelatin.

of various commercial tannin materials, together with the oxalic acid equivalents of the total oxidizable matters, and of the tannin as precipitated by Procter's and Hunt's methods.[1] The difference between the results obtained by these two methods is attributed by Hunt to the precipitation of gallic acid by the saturated brine employed by Procter.

Material.	Insoluble Matter.	Total Extract.	In terms of Oxalic Acid.		
			Total Oxidizable Matters.	Tannin, Procter.	Tannin, Hunt.
"Pure tannin,"	. .	. .	135.76	122.44	121.93
English oak-bark, . . .	66.15	18.38	15.70	13.54	11.97
Canadian hemlock-bark,	75.25	13.96	9.03	7.46	7.08
Larch-bark, ...	60.80	20.64	8.20	7.17	6.15
Mangrove-bark, ...	49.70	26.60	31.35	29.71	28.48
Alder-bark, ...	68.00	19.36	8.27	6.15	5.73
Valonia, ...	46.05	38.50	37.41	35.24	30.50
Myrabolams, ...	.	42.80	48.23	38.43	38.00
Sumac, ...	47.77	44.10	42.53	34.30	31.46
Turkish blue galls, . .	36.35	48.40	73.38	65.83	59.96
Aleppo galls, ...	14.32	68.80	98.85	87.82	83.05
Wild galls, ...	54.17	31.70	26.21	18.75	16.56
Divi-divi, ...	29.90	54.38	66.68	62.62	61.22
Pomegranate rind, . . .	49.50	41.00	27.58	24.18	23.12
Tormentil root, ...	67.95	19.70	22.27	20.98	20.68
Ratanhy root, ...	66.00	18.80	22.27	20.15	19.30
Pure Indian tea, . . .	53.40	34.46	23.06	18.65	17.40
Pure China tea, ...	62.60	24.50	18.03	14.21	14.09
Cutch, ...	4.75	61.60	57.65	51.95	44.24
Gum kino, ...	1.00	79.30	66.39	59.55	51.55
Hemlock extract, . . .	. .	48.78	35.16	33.17	30.98
Oak-wood extract, . . .	. .	37.78	33.49	26.90	23.86
Chestnut extract, . . .	. .	50.28	39.77	32.63	28.88
Quebracho extract, . .	. .	49.00	48 22	44.45	40.84
Tan-liquor (sp. gr. 1.030),	. .	6.01	4.84	3.14	2.10
Spent liquor (sp. gr. 1.0165), ...	. .	3.10	1.40	0.37	0.25

[1] Hunt states in the same paper that treatment with gelatin and salt does not remove all that is of tanning value from solutions of gambier and allied materials, and hence he recommends the removal of the tannin in such cases by means of purified skin-shavings. These he adds in the proportion of 5 grammes to 100 c.c. of a 1 per cent. gambier solution, and after twelve hours filters and titrates the filtrate with permanganate in the usual way. The following results were obtained:

	Insoluble Matter.	Total Extract.	In terms of Oxalic Acid.	
			Total Oxidizable Matter.	Absorbed by Skin.
Cube Gambier,	5.31	74.40	70.12	51.07
Sarawak "	3.67	70.70	63.13	47.09
Bale "	1.40	63.54	56.00	43.70

A few years since, the permanganate process of determining tannin was submitted to a careful examination by a commission of German chemists. After reviewing earlier methods they recommended the following modifications of the permanganate process for general adoption:—1. That the *permanganate* solution contain 10 grammes of $KMnO_4$ in 6000 c.c. 2. That the *indigo-solution* should be made by dissolving 30 grammes of air-dry sodium sulphindigotate in 3000 c.c. of dilute sulphuric acid (1 : 3), 3000 c.c. of water added, the whole shaken till dissolved, and the liquid filtered. 20 c.c. of this solution in 750 c.c. of water should be used in each titration, and should reduce about 10.7 c.c. of the permanganate solution. 3. *Hide powder* is substituted for the ordinary gelatin solution. It must be white, and in a fine woolly state of division, and should yield to cold water no substance capable of reducing permanganate.

Instead of adding the permanganate solution drop by drop, the commission recommend (with very doubtful advantage) that an addition be made of 1 c.c. at a time, and the mixture vigorously stirred for five or ten seconds after each addition. As soon as the liquid has become bright green, two or three drops at a time should be cautiously added with stirring, till the liquid is pure yellow. The results obtained by the "1 c.c. method" differ considerably from those obtained by the ordinary or "drop method," which was that employed by Neubauer and Oser for the determination of the reduction co-efficients of tannins. It has, however, been shown by H. R. P r o c t e r (*Jour. Soc. Chem. Ind.*, v. 79), that the results are more influenced by the rapidity of mixing than by actual time, and that the 1 c.c. method, while it always gives a higher consumption of permanganate than the drop method, is even more affected by variations in stirring.[1]

To determine the oxidizable matters "not tannin," 50 c.c. of

[1] Procter points out that the limit of the reaction is not a complete oxidation of the organic matter, but only a partial one of the bodies more readily oxidizable than indigo; and hence towards the end of the operation, when the indigo has become scarce, the permanganate is partially consumed in further oxidizing the products of the normal reaction; and that this is least the case when the permanganate is added slowly and rapidly mixed with the liquid, so as to bring it into immediate contact with the remaining indigo. Procter obtained very uniform results by the use of a stirrer consisting of a perforated porcelain disc, which was worked up and down in the beaker by means of attached glass rod; and the results were still further improved by attaching a capillary jet to the point of the burette, and allowing the permanganate to run in steadily throughout the titration.

the infusion should be digested in the cold with 3 grammes of the hide powder (previously moistened with water, and well squeezed in linen). The liquid is frequently agitated during eighteen to twenty-four hours, and is then filtered, and 10 c.c. titrated in the usual way.[1]

F. S i m a n d has recommended the use of the purified gelatinous matter of bones as acting more quickly than hide powder (*Jour. Soc. Chem. Ind.*, i. 509). Tubular bones, freed from joints and marrow, are crushed and soaked for two days in a 5 per cent. solution of soda, then thoroughly washed with water, reduced to smaller pieces, and treated with dilute hydrochloric acid until softened. They are then again washed, and passed through a small grinding machine while still wet. The comminuted mass is treated with very dilute hydrochloric acid, thoroughly washed, pressed and dried.

E. B. (*Jour. Chem. Soc. Ind.*, vi. 51) suggests the use of ferric acetate instead of gelatin for precipitating tannin. The process has only been tried on gall-tannin, and F. G a n t t e r (*Journ. Chem. Soc.*, liv.) doubts its accuracy in this case.

Other operators have recommended the use of an ammoniacal solution of copper for removing the tannin. This modification is not capable of general application. *Sumac*, however, is a tanning material which may be advantageously precipitated by ammoniocupric acetate,[2] with titration of the solution by permanganate and indigo before and after the treatment.[3]

[1] The International Association of Leather-Trades Chemists recommend: "That the 'bell form' of filter, as described by Prof. Procter, be adopted, and that not less than 5 grms. of hide-powder be used, and that the filtrate be rejected so long as it gives a turbidity with a clear tanning solution. The filtrate may be used for the determination of non-tannins so long as it gives no reaction with hide-powder water. That 50 c.c. or less quantity of detannized solution be evaporated in a weighed basin on a water-bath, and then dried till constant in an air oven, at a temperature of 100° to 105° C., or *in vacuô* not exceeding 100° C."

[2] M e y e r (*Chem. Zeit.*, xiv. 1202) says that the precipitation with copper acetate yields excellent results if the precipitation takes place in a hot solution, and washing with hot water must follow immediately. The precipitate is dried at 110° C., weighed, and ignited to CuO. From the weight of the total precipitate, four-fifths of the weight of the resulting copper oxide is deducted, which gives the total tannin.

[3] By this process, I. M a c a g n o (*Chem. News*, xli. 63) found that the superior side of sumac leaves was considerably richer in tannin than the lower, the proportion in old leaves being less than in young. The results varied from 8.77 per cent. of tannin in the lower side of old, to 25.82 per cent. in the superior side of young leaves.

N. H. D a r t o n (*Jour. Amer. Chem. Soc.*, May, 1882) employs ammonio-sulphate of copper in the following manner:—Twenty grammes of *hemlock-bark*, or an equivalent amount of other tannin material, is extracted first with cold and then with several quantities of boiling water. The mixed infusions are treated with 25 c.c. of dilute sulphuric acid (1 : 10), the liquid filtered, and the filtrate rendered slightly alkaline with ammonia, any precipitate being filtered off. A further quantity of 25 c.c. of dilute sulphuric acid is then added, and the liquid made up to 1 litre. 100 c.c. of this solution is treated with an equal measure of a solution of cupric sulphate (containing 1¼ per cent. of the salt), to which sufficient ammonia has been added to dissolve the precipitate first formed. The liquid is passed through a dry filter, and a definite measure of the filtrate neutralized and titrated for "not tannin" with indigo and permanganate in the usual way. H. R. P r o c t e r states that the preliminary treatment with acid and ammonia is unnecessary in the case of *valonia* (and probably in that of oak-bark), and that the process gives results practically identical with the improved gelatin method, while it is much less troublesome. With *chestnut extract* the results are satisfactory, provided the preliminary treatment be omitted, as this removes 75 per cent. of the matter precipitable by gelatin, and cutch behaves similarly. On the other hand, a sample of *larch extract* which tanned well, and showed 18 per cent. of tannin by the gelatin method, gave *no* precipitate with the ammonio-cupric solution. This peculiarity would allow of the estimation of valonia-tannin in presence of larch-tannin, and the same principle might be utilized in other cases.

When applicable, the copper process has the advantage that the precipitate may be washed with a solution of ammonium carbonate, dried, and weighed. Or the precipitate may be ignited, the residue moistened with nitric acid, and re-ignited, and the cupric oxide weighed. Its weight, subtracted from the weight of the precipitate previously found, gives that of the tannic acid with which it was combined, or the latter may be found by multiplying the weight of CuO by 1.034. This factor probably applies only to gallotannic acid.

A. C a r p e n é (*Jour. Chem. Soc.*, xxviii. 1054) recommends, for the determination of the tannin in *wine*, the use of a solution of ammonio-acetate of zinc containing a large excess of ammonia, which reagent has the property of forming with œno-tannin a tan-

nate of zinc quite insoluble in water, in ammonia, and in excess of the reagent itself; while it gives no precipitate with alcohol, malic or tartaric acid, tartrates, glycerin, gelatin, albumin, or the iron salts of organic acids.   With gallic and succinic acids, glucose, and salts of aluminium it forms precipitates soluble in excess of the reagent and in ammonia.

On treating the wine with an excess of ammoniacal zinc acetate, a precipitate is formed, consisting of zinc tannate mixed with a small quantity of coloring matter.   The wine is heated nearly to boiling to agglomerate the precipitate, which, after cooling, is filtered off and washed with a little boiling water, to remove adherent coloring matter.   The precipitate is dissolved in dilute sulphuric acid, and the solution so obtained titrated with standard permanganate and indigo, as indicated on page 73.   The results by this method are stated to be very accurate, when applied to wine, but Kathreiner found that with ordinary tannin-matters the figures were very inconstant.

DETERMINATION OF THE WEIGHT OF TANNIN ABSORBED BY HIDE.

Instead of precipitating or absorbing the tannin from an infusion by means of gelatin, and ascertaining the difference in the reducing power of the liquid before and after the operation, several operators have proposed to note the difference in the solid matter contained in the liquid.   In doing this there is considerable practical difficulty. Thus the gelatinous matter must be so pure that it will not yield to water sufficient soluble matter to vitiate the result: the solution must be very dilute, or the whole of the tannin will not be absorbed; and special means must be taken to bring the gelatin in contact with the tannin, as otherwise the outer portions become swollen and impervious to the liquid, at least within any reasonable time.   The last difficulty may be avoided by using finely powdered hide to absorb the tannin, and adding it in small successive portions at intervals of ten or twelve hours,

Fig. 1.

whereby the portions first added are made to do the greater part of the work, and the later additions effect the removal of the last
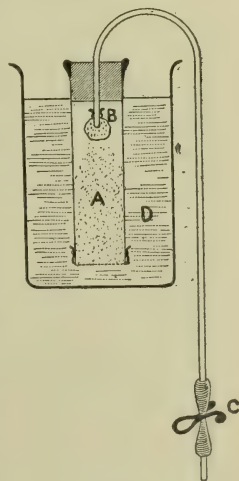
of the tannin from the liquid. A more rapid plan is that of H. R.
P r o c t e r, who operates as follows:—A piece of stout glass tube
about 4 inches long and 1 inch in diameter (Fig. 1), is fitted in
one end with a perforated cork carrying a syphon tube, the larger
leg of which is from 12 to 15 inches in length. The end of the
shorter limb projects through the cork, and is covered with a little
tuft of cotton wool and a piece of muslin to prevent the hide pow-
der from passing into it. The wide tube is filled with about 5
grammes of hide powder, which is well shaken but not rammed
in, and the open end is then covered by a circle of muslin, which
is secured by an india-rubber band. The wide tube is then immersed
in 100 c.c. of the tannin infusion (which should not contain less than
1 per cent. of tannin) contained in a beaker, and when the hide
powder is thoroughly soaked the syphon is gently sucked so as to
cause the liquid to pass over into a flask placed to receive it.
When a volume of 50 c.c. has collected, it should be evaporated
to dryness at 100° and the residue weighed. 50 c.c. of the orig-
inal tannin infusion is similarly evaporated to dryness, when the
difference between the weight of the two residues will be the
weight of tannin, etc., absorbed by the hide from 50 c.c. of the
infusion. The figure thus obtained requires to be corrected by the
result of a blank experiment on hide and distilled water alone, for
even the most carefully prepared hide gives a residue of 30 to 40
milligrammes from 5 grammes. This process, which is perhaps
the most rational yet devised for assaying tanning materials, is un-
fortunately wanting in accuracy in presence of much gallic acid,
which Procter found to be absorbed by hide from a 1 per cent. so-
lution to an extent equal to 78 per cent. of the whole; an unsta-
ble compound with gelatin being apparently formed which in
practical working would have been subsequently decomposed by
the excess of tannin.[1] Hence, for the assay of tanning materials
containing much gallic acid, the oxidation method, in which a so-
lution of gelatin is employed, is to be preferred to that of absorp-
tion by hide.[2] The hide process is in constant use at the Vienna

[1] The gravimetric method of estimating tannin is also open to the objection that
a number of other substances, such as metallic salts, phenols, alkaloids, picric
acid, etc., are precipitated by hide, and are therefore included in the difference
between the total solids and the solids not tannin.

[2] According to T. C. P a l m e r (*Jour. Soc. Dyers, &c.*, iii. 175), sumac extracts
give too high a result by the gelatin precipitation process, owing to the co-precip-
itation of pectinous matter. The error may be avoided by first dissolving the

Versuchs-station für Leder-industrie, where the error due to the presence of gallic acid has not been found of much practical moment. The rejection of the first 30 c.c. of the filtrate reduces it considerably, and also greatly lessens the effect of the soluble matter in the hide powder.[1]

H. D i e u d o n n é (*Jour. Soc. Chem. Ind.*, v. 549) has proposed to ascertain the density of the infusion before and after the absorption by means of a delicate hydrometer, instead of weighing the residues obtained on evaporating equal volumes to dryness. He uses a special hydrometer, on which 1° Baumé is divided into hundredths (!), and he gives a table of densities of solutions of gallotannic acid. The trifling saving of time effected by ascertaining the density of the infusions, instead of evaporating them to dryness, would be more than counterbalanced by the uncertainty that all tannins have the same solution-density as gallotannic acid.[2] The suggestion is practically a revival of the obsolete process of H a m m e r. According to this observer, for concentrations below 5 per cent., gallotannic acid has a solution-density of .004. Above that strength the increase is slightly more rapid, a 10 per cent. solution having a density of 1.0406, and 15 per cent. of 1.0614, while a 20 per cent. solution has a density of 1.0824. Hence each 0.1 gramme of gallotannic acid present in 100 c.c. of its aqueous solution may be regarded as increasing the density by 0.0004.

Under ordinary circumstances, the direct observation of the increase in the weight of the hide, or other gelatinous substance employed, is impracticable, but purified catgut has been used, with apparent success, by A. G i r a r d for the estimation of the tannin and coloring matter of *wine*[3] (*Jour. Soc. Chem. Ind.*, i. 464.)

extract in alcohol, evaporating the filtered liquid, and re-dissolving the residue in water. With such treatment, at any rate if repeated, the precipitation process gives results agreeing with the absorption method.

[1] The International Conference of the Chemists connected with the Leather Industry have adopted the hide-powder method for the estimation of tannin.

[2] If any such method be adopted, the use of a Westphal balance is preferable to that of a hydrometer. By comparing the original and filtered infusion side by side far better results might be obtained, and if the experiments were accompanied by determinations of the solid matter corresponding to the densities observed, a useful series of tables might be constructed.

[3] Thick catgut (violin string) previously freed from oil by treatment with ether, is the best material to use, the quantity employed for 100 c.c. of wine being from 3 to 5 grammes, according to the character of the sample. The membrane should be obtained before being twisted or otherwise treated. It should be dried and

W. Schmitz-Dumont (*Zeit. für öffent. Chemie.*, iii, 209)
proposes as a substitute for hide powder formalin-gelatin prepared
in the following way: thick filter paper is saturated with a 10 per
cent. solution of gelatin and dried. It is then immersed for 24
hours in a 2 per cent. solution of formalin, and afterwards dried
at 95°. It is then cut into strips and reduced to powder by grind-
ing, and again treated with formalin solution for 24 hours. It is
then dried at 100°. In order to free the preparation from trioxy-
methylin it is digested in hot water until the washings give no
formaldehyde reaction with alkaline resorcin. The powder is then
dried on a water-bath and is ready for use.

Other Methods of Determining Tannins.

The direct weighing of the precipitate produced by gelatin in a
solution of tannin was first suggested by Sir H. Davy, who
stated that the precipitate contained 40 per cent. of gallotannic
acid. The method has been more recently employed by Stoddart,
Macagno, Günther, Johansen, Lehmann, and others, who differ
widely in their statements as to the composition of the precipitate.[1]
It undoubtedly varies greatly in composition according to the
strength of the solution and other circumstances, besides which it
is soluble in excess of gelatin solution and very difficult to wash
free from alum or other salts employed to curdle it. The variable
nature of the precipitate is liable also to vitiate the results obtained
by employing a gelatin solution volumetrically, to say nothing of

soaked in sulphurous acid to preserve it. The catgut is weighed, softened by
soaking in water for five hours, and immersed in the wine for twenty or forty-
eight hours, or until the liquid is completely decolorized. The catgut is then
removed, washed two or three times with water, pressed between folds of blotting
paper, dried at 35° to 40° C. in an open dish, and afterwards at 100° in a vessel
which can be closed. The increase in weight gives the quantity of coloring and
astringent matters in the wine employed for the test. This process appears to be
too slow for the assay of ordinary tannin-matters.

[1] Assuming the precipitate to contain 40 per cent. of tannin, Macagno obtained
with sumac pretty constantly 53 per cent. of the results yielded by permanganate.
Günther found that 100 parts of gelatin precipitated 77 of gallotannic acid, 132
of catechu-tannin, 130 of kino, 130 to 132 of ratanhia, 130 of oak-bark, or 168 of
tormentilla-tannic acid. 100 parts of gelatin combined with 120 of dry gallotan-
nic acid, according to Johansen, and with 130 of catechu-tannic acid according to
Lehmann. Quite recently, C. Böttinger has found the precipitate produced
by gallotannic acid to contain 16.5 per cent. of nitrogen, corresponding to 34 per
cent. of tannin; while oak-bark tannin gave a precipitate containing 9.5 per cent.
of nitrogen, corresponding to 42.7 per cent. of tannin (*Jour. Chem. Soc.*, liv. 614).

the difficulty of ascertaining the end of the reaction. But L e h-
m a n n has shown that the liquid may be diluted within certain
limits without notably affecting the result, while the clarification
of the liquid can be effected by adding powdered glass or barium
sulphate, and vigorously stirring. He dilutes the tannin infusion
with an equal volume of saturated aqueous solution of ammonium
chloride, and titrates with a 1 per cent solution of gelatin in cold
saturated ammonium chloride. The end of the reaction is ascer-
tained by filtering a few drops of the liquid and testing it with a
solution of gelatin on a watch-glass placed on a black surface.
Catechu-tannic acid is said to give good results in this way, 1 c.c. of
the gelatin reagent representing 0.139 gramme of the tannin.
J o h a n s e n recommends that a little chrome-alum should be
added to the ammonium chloride solution.

A modified method of determining tannin by precipitation with
gelatin has been recently described by C o l l i n and B e n o i s t
(*Jour. Soc. Dyers, &c.*, iv. 62), and appears to merit a careful trial.
They employ an aniline dye in conjunction with gelatin, and oper-
ate in presence of calcium acetate.[1] The end of the operation is
indicated by the decolorization of the liquid, the dye being precip-
itated together with the gelatin.

A solution of t a n n i n is made by dissolving 5 grammes of dry
and absolutely pure tannic acid in water, adding 0.5 c.c. of a 10
per cent. solution of mercuric iodide dissolved in its own weight of
potassium iodide, and diluting the liquid to 1 litre. A weight of 5
grammes of g e l a t i n is dissolved in 1 litre of hot distilled water,
the liquid boiled, and sufficient white of egg added to make it clear.
After cooling, 0.5 c.c. of the mercuric iodide solution is added
and sufficient caustic soda to render the liquid slightly alkaline.
50 grammes of pure and dry calcium acetate is dissolved in 1
litre of water, and the filtered liquid treated with a few drops of
the mercuric iodide solution. This appears to act as a perfect pre-
servative of the solution, no alteration being perceptible even after
four months.

For the assay of tannin infusions which are not colored, a 1 per
cent. solution of pure methylene blue is used. For colored tannins
or extracts either a 4 per cent. solution of Nicholson's blue BB, or
a 1 per cent. solution of blue-black NBI.

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[1] The use of magenta as an indicator was previously suggested by Wagner, but
was found useless from the fact that it was freely absorbed by the precipitate of
tannate of gelatin.

For the determination a flask is used, having a capacity of about 60 c.c., and a neck 3 cm. in diameter.   1 c.c. of gelatin solution, two drops of blue solution and 5 c.c. of calcium acetate are measured into the flask, which is then filled to the neck with distilled water at a temperature of 75° to 80° C., by means of a burette capable of delivering at 40 drops to 1 c.c.[1]   A little of the standard solution of tannin is added, when the flask is closed and shaken. A precipitate is formed which rapidly rises to the surface of the liquid, and the addition of the tannin is continued drop by drop with agitation between each addition until the solution becomes colorless.   The process is then repeated with a solution of the tannin-matter to be assayed, which, if acid, should previously be nearly neutralized by the cautious addition of caustic soda.

The method has been tried under various conditions.   Alterations in the strength of the tannin solutions; the presence of other organic matters, such as lactates, butyrates, gallates, and gallic acids; and all the salts that accompany tannin as it occurs in commerce, have little or no influence on the results.   The operation is only spoilt when a large proportion of gallic acid is present, and this difficulty can be got rid of by adding a known measure of the standard tannin solution to the solution to be assayed, and subsequently making the requisite correction.

A method of assaying *tea*, originating with the a u t h o r (*Chem. News*, xxix. 169, 189), was based on the precipitation of the tannin from a hot solution by a standard solution of lead acetate, the end of the reaction being ascertained by filtering a few drops of the liquid and testing it with ammoniacal ferricyanide.   The method was selected partly because the indications included any gallic acid which might be present, and hence is not suited for the assay of tanning materials without some modification.[2]

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[1] The authors used specially constructed burettes.   An ordinary burette with glass-tap would answer the purpose, if a special nozzle of drawn-out glass tube were attached to it by india-rubber tubing.   Apparently it would not be difficult to modify the manipulation so as to employ larger quantities or more dilute solutions, and thus avoid the necessity of using a special burette.

[2] M. V i l l o n (*Jour. Soc. Chem. Ind.*, vi. 388) states that gallic acid is not precipitated by lead acetate, but the author has proved that only a minute trace remains in solution.   It seems probable, as suggested by Guyard, that by using a solution of acetate of lead containing a considerable quantity of free acetic acid it might be possible to precipitate tannic acids (and coloring matter) while leaving gallic acid in solution, and then, by treating the lead precipitate with dilute sulphuric acid, a solution would be obtained in which the tannic acid could be

R. J a c k s o n (*Chem News*, l. 179) has proposed to agitate tannin infusions with lead carbonate, filter after a few hours, and calculate the tannin from the loss of gravity, assuming a 1 per cent. solution of all kinds of tannin to be 1.0038.

In G e r l a n d ' s process, the tannin is precipitated by a standard solution of tartar-emetic (2.611 grammes per litre), in presence of ammonium chloride, which prevents the co-precipitation of gallic acid.   The assay of *sumac* by this method yielded J. Macagno results which were constantly two-thirds of those given by titration with permanganate.   The tendency of the antimonial solution to change may be obviated by the addition of methylated spirit to the solution (or probably by carbolic acid).   Some tannins (*e. g.*, those of catechu and horse-chestnut) are not precipitated by tartar-emetic.

R i c h a r d s and P a l m e r (Silliman's *Amer. Jour. Science*, [3], xvi. 196, 361) substitute acetate for the chloride of ammonium in Gerland's process, and ascertain the point of complete precipitation of the tannin by testing a drop of the clear supernatant liquid on a hot porcelain plate with solution of sodium thiosulphate, which will produce an orange precipitate if the antimony is in excess.   The standard solution of tartar-emetic contains 6.730 grammes of the dried salt per litre; 1 c.c. of this solution is equivalent to 0.01 gm. of tannin.

The estimation of tannin by precipitation with an ammoniacal solution of copper has already been described.

A. C a s a l i (*Jour. Soc. Dyers, etc.*, i. 66) has proposed to determine tannin by precipitation with a solution of ammonio-sulphate of nickel.   A volume of solution (1 c.c.) which will precipitate 0.01 gramme of gall-tannin is stated to be equivalent to 0.01497 of oak-bark tannin.

F. B e c k e r has described a method of determining tannin by precipitation with a solution containing 5 grammes of methyl-violet per litre (*Jour. Soc. Dyers, etc.*, i. 180).   50 c.c. measure of this solution is diluted with 450 c.c. of water at 50° C., and a 1 per cent. solution of pure gallotannic acid run slowly in, with continual stirring, until the coloring matter is completely precipitated, a point readily ascertained by filtering a small sample.   A similar experiment is then made with an infusion of the tanning material

determined by indigo and permanganate.   This direction seems to the author the most hopeful one in which to work with a view of devising a rapid and direct process for the determination of tannins.

to be tested.   The process is said to be well adapted for the assay of *sumac,* and would probably be found useful in most cases where the tannin is intended to be employed in dyeing.

O s t e r m e y e r, improving on a suggestion of W a g n e r, has proposed to determine tannin by a standard solution of cinchonine colored with magenta, the end of the reaction being indicated by the pink tint acquired by the solution (*Chem. News*, xl. 181). Gallic acid is not precipitated by cinchonine.   Some observers report unfavorably of this process, and state that in certain cases the liquid acquires a red tinge long before the tannin is precipitated. The alkaloid solution contains 4.523 grammes of sulphate of cinchonine, with 0.5 gramme sulphuric acid and 0.1 gramme fuchsine in 1 litre; each c.c. of this solution precipitates 0.01 gramme of tannic acid.

F. J e a n (*Jour. Soc. Chem. Ind.*, v. 179) has described an ingenious process of determining tannin, based on the volume of the infusion requisite to render a solution of iron opaque.   The operation is conducted in a beaker $8\frac{1}{2}$ centimetres in diameter, placed in a good light on a black cloth, having on it a small circle of white paper about 5 cm. in diameter.   5 c.c. measure of a solution of iron, containing 14 grammes of ferric chloride and 10 c.c. of hydrochloric acid per litre, is run into the beaker, and 200 c.c. of water added.   A 0.1 per cent. solution of tannin is then dropped in with constant stirring.   The operation is finished when the disk of white paper is wholly invisible after the liquid has come to rest, which in the case of pure gallotannic acid occurs when 11.6 c.c. of the solution has been added.   In comparing tanning materials with this it is simply necessary to take care that the infusions are approximately of the same richness in tannin, and this may be attained by extracting 1.5 gramme of European bark, 1.0 of African bark, 0.5 of quebracho, 0.5 of sumac, or 0.25 gramme of catechu; and diluting the liquid to 100 c.c.   The determination can be made very rapidly, and is said to be accurate to $\frac{1}{2}$ per cent.   By subsequently repeating the experiment with a solution which has been treated with hide, the error caused by gallic acid may be eliminated.

E. D u r i e n (*Year-Book Pharm.*, 1886, iii.) has proposed to determine tannin by adding acetic acid and ferric chloride to the infusion, and then dropping in a standard solution of bleaching powder (5 grammes per litre) till the color of the liquid changes suddenly to a rose-brown tint.   Sugar was found not to affect the result, but gallic acid was ignored.

F. M u s s e t (*Chem. News*, li. 42) has described a method of ti-
trating tannin by oxidation with iodine. 100 c.c. of a 1 per cent.
of bark is treated with 20 c.c. of decinormal solution of iodine
(12.7 grammes per litre), the flask filled to the neck with warm
air-free water, and carefully closed. After twelve hours, the free
iodine is reduced by standard thiosulphate solution, which should
be added somewhat in excess, and the liquid titrated back with
decinormal iodine and starch. By operating in a similar manner
on a solution which has been treated with gelatin, the disturbing
effect of gallic acid and other "not tannin" matters is ascertained,
and can be allowed for.

A. M o u l l a d e (*Jour. Pharm. Chim.*, xxii. 153) describes a
method of determining tannin by means of iodine in the presence
of sodium bicarbonate. Carbon disulphide is used as an indica-
tor. The iodine solution should contain 5.2 grammes of iodine
and 7.6 grammes of potassium iodide per litre; the sodium bicar-
bonate solution is 1:10. To 10 c.c. of a tannin solution 30 c.c. of
the bicarbonate solution are added, together with 2–3 c.c. of carbon
disulphide. The iodine solution is introduced from a burette until
a blue color appears. Several titrations are necessary to insure
good results. In the presence of substances whose behavior is
similar to tannin, two experiments are necessary, in one of which
the tannic acid is precipitated by the gelatin; the difference between
the two titrations corresponds to the tannin present.

D r e a p e r (*Jour. Soc. Chem. Ind.*, 1893, 412) gives a volumetric
method for tannic and gallic acids by direct precipitation with a
copper salt, using an outside indicator, preferably potassium ferro-
cyanide. A standard solution of copper sulphate is added to the
tannin solution in the presence of a known quantity of barium
carbonate. The latter immediately forms an insoluble precipitate
with the free acid which is liberated, and also aids in consolidating
the precipitated copper salts, causing the precipitation to proceed
with great nicety. The copper sulphate solution should contain
30 grammes of the crystallized salt in 1 litre of water, and the ba-
rium carbonate should be free from calcium salts, as these would
precipitate some of the tannic acid.

E. G u e n e z (*Compt. rend.*, cx. 532) gives the following volu-
metric method for the estimation of tannin. A standard solution
is prepared containing 12 grammes of tartar-emetic and 1 gramme
of Poirier's green 4JE to 1 litre of water. The solution of tannin
is run from a burette into 20 c.c. of the boiling colored solution

until it is completely decolorized. The standard solution may be fixed on a solution of pure oak-gall tannin of known strength. Gallic acid does not interfere with the process.

L. R o o s (*Jour. Pharm. Chim.*, 1890, 59) gives a volumetric method adapted to the determination of tannin in wines. A 10 per cent. solution of tartaric acid is used, made faintly alkaline with ammonia; neutral lead acetate is then added until the precipitate no longer dissolves, when the solution is filtered. Tannin is said to be completely precipitated by this solution, sodium sulphide being used as an indicator. About 25 c.c. of the wine are taken for analysis and made slightly alkaline with ammonia.

P. W i l h e l m (*Rev. gén. des mat. colorantes*, Aug., 1898) describes a method of estimating tannin by adding the tannin solution to a known volume of standardized methylene blue solution (containing a small quantity of ammonia to neutralize the free mineral acid generated) until the reaction is complete. The methylene blue solution should contain 12.5 grammes dissolved in 1 litre of water, and the coloring matter should be free from zinc. The tannin solution is titrated into the methylene blue solution to which a little ammonia has been added. The end point is determined by spotting from time to time on stout filter paper. When all the blue has been precipitated, the back of the spotted filter paper remains colorless. The process has given results accurate within 2 per cent.

L. V i g n o n (*Compt. rend.*, cxxvii. 369) describes a method for the estimation of tannin by the use of silk. He claims that silk free from gum absorbs tannin readily and completely from solutions of tannin materials at 50° Bé., but does not absorb gallic acid, glucose, etc. The tannin may be estimated either by the increase in the weight of the silk, or by the difference in the proportion of solid matters in the solution before and after treatment with silk, or by titration with permanganate. The accuracy of this method, however, the author has found to depend on the nature of the tannin material employed, as silk does not appear to absorb all tannin materials in the same proportion.

A. S e y d a (*Chem. Zeit.*, xxii. 1085) describes a delicate test for tannins. He has noticed that if gold chloride is added to a very dilute solution of tannin a clear purple liquid is obtained. The principal use of this test is to determine the presence of tannin in highly colored extracts. Before applying the test they are diluted until practically colorless, the gold chloride is added, and the liquid allowed to stand for half an hour.

S. T. H i n s d a l e (*Chem. News*, 1890) gives the following colori-
metric method for estimating tannin in bark which appears to have
a practical value.   The following solutions are prepared: Dissolve
0.04 gramme potassium ferricyanide in 500 c.c. water, and add to
it 1.5 c.c. liquid ferric chloride; this is called the iron mixture.
Dissolve 0.04 gramme "pure tannin" (gallo-tannic acid), which
has been dried at 100° C., in 500 c.c. water; call this the tannin
solution.   0.8 gramme of the bark is exhausted with boiling
water, and the extract made up to 500 c.c. with cold water.   Place
six 2 ounce beakers on a white surface, and in one of them place
5 drops of the bark infusion, and in the others put 4, 5, 6, 7 and
8 drops of the tannin solution.   Add to each 5 c.c. of the iron
mixture, and then make a further addition of 20 c.c. of water to
each after about one minute; and within three minutes observe the
shades of color.   Then the number of drops of tannin solution
used in the beaker which corresponds in shade of color to the
beaker containing the bark infusion indicates the percentage of
tannin in the bark.   The results are necessarily in terms of com-
mercial gallo-tannic acid, and not in those of pure tannin or of
the particular tannin in the material assayed.   For substances
containing over 10 per cent. of tannin, the infusion should be
proportionately diluted.

Examination of Tan-Liquors.

Besides determining the tannin and oxidizable substances in tan-
liquors, it is frequently desirable to obtain further information as
to the proportion and nature of the free acids present.   It is an
error to suppose that the principal free acid of tan-liquors is gallic
acid, as this is not present in pure bark-yards.   The most abun-
dant acid is usually acetic, though butyric, lactic, and other acids
produced by fermentation are frequently present.

The total free acid may be ascertained by titrating the filtered
liquid (previously clarified, if necessary, with kaolin) with lime-
water.   The end of the reaction is indicated by the production of
a permanent turbidity, showing that the acids which held the cal-
cium tannate in solution are neutralized.   By titrating another
portion of the liquor with lime-water, using methyl-orange as an
indicator, the proportion of strong acids capable of producing
"plumping," or swelling of the leather, will be roughly ascer-
tained.   Sulphuric acid is sometimes added for this purpose.

A more accurate and elaborate method of assaying tan-liquors

has been described by K o h n s t e i n and S i m a n d (*Jour. Chem. Soc.*, xlviii. 935). To determine the *volatile organic acids* (acetic, butyric, etc.), 100 c.c. measure of the liquor is distilled to 30 c.c., the residue made up with water to the original bulk and again distilled, and the process repeated till the total distillate measures 300 c.c., when it is titrated with standard caustic alkali and phenolphthalein, and the acidity expressed in terms of a c e t i c a c i d. By adding sulphuric acid and water to the contents of the retort, and again distilling and titrating the distillate, the combined acetic acid may be determined.

Another portion of the liquid (80 or 100 c.c.) is shaken with 3 to 4 grammes of freshly-ignited magnesia, quite free from carbonate and lime. The mixture is left for some hours with frequent agitation, when the brown or dirty green color will have disappeared, and the filtered liquid will be nearly colorless, neutral, and free from tannin. The magnesia in solution is determined in an aliquot part of the filtered solution, and will be equivalent to the total free acids of the liquor, exclusive of the tannic acid, which is completely precipitated together with the coloring matter. Another portion of the filtrate is evaporated to dryness, and the residue *gently* ignited. The ash is moistened with carbonic acid water and dried. It is then boiled with distilled water, and the solution filtered. The magnesia remaining insoluble corresponds to that which existed in the solution as magnesium salts of *organic acids*, and may be determined gravimetrically as pyrophosphate, or dissolved in standard acid and titrated with alkali and methyl-orange or litmus. By dividing the percentage of acetic acid previously found by 3, and subtracting this figure from the percentage of MgO, the weight of the latter corresponding to the *non-volatile organic acids* of the liquor will be found; and 4.5 times this amount will be their equivalent of l a c t i c a c i d. The magnesia contained in the aqueous solution of the ash is equivalent to the free *sulphuric acid* originally present.

The liquors of a set of seven handlers, in a Continental upperleather tannery in which larch-bark was used, showed, by the above process, in grammes per 100 c.c. :—Total acids reckoned as acetic, from 0.20 to 0.68; volatile acids, 0.05 to 0.46; and fixed organic acids reckoned as lactic acid, 0.05 to 0.59.

In the estimation of tannin in acid liquors, M ü r k a t z has recommended neutralizing the acid with barium carbonate, claiming that no loss of tannin is caused. But others have shown (B a r t e l,

Dingl. Polyt. Jour., 1891, p. 233) that a considerable loss of tannin does occur in neutralizing with either barium carbonate or sodium hydrate, and consequently such a treatment is not permissible.

The hide-powder process for the gravimetric estimation of tannin is not applicable to the testing of acid liquors, because the hide absorbs a certain proportion of the acid which is thus estimated as tannin.

J. Pässler (*Dingler's Polyt. Jour.*, ccxcv, 141) claims that if the greater proportion of the volatile acid has been removed previously by repeated evaporations, the hide-powder process can usually be applied to the testing of tan-liquors containing acetic and lactic, and similar acids, without serious error; and that the results are sufficiently accurate for due control of the tannin process, and far more accurate than those obtained by the Löwenthal or Mürkatz processes.[1]

Estimation of Sugar-Content of Tanning Materials.

For a solid tanning material, a weighed quantity of the ground substance is extracted with water (1 litre at 100° C.).   600 c.c. of the filtered extract are concentrated to 200 c.c., and the tannins, etc., are precipitated from this solution by the addition of 20 c.c. of lead acetate solution; after 15 minutes, during which time the flask has been frequently shaken, the liquid is filtered through a dry filter, and to 100 c.c. of the filtrate, 10 c.c. of sodium sulphate solution (equivalent to the lead acetate solution) are added; the

[1] F. Andreasch (*Der Gerber*, xxiii. 111) in a study of the fermentation phenomena in tan liquors, shows that the acidity of the liquor is due to the following causes:

1. Putrefactive bacteria from the hides, bates, etc., accommodate themselves to the acid reaction of tan liquors; they dissolve certain nitrogenous constituents of the hide, and thereby furnish the chief nutriment for the more specific acid-producing bacteria.   In liquors which are in use, the production of acid is proportional to the hide substance present, provided sufficient quantity of carbohydrates are present.

2. Acetic acid, which in fresh tan liquors is the chief acid, is always formed by two separate processes: (1) the production of alcohol by yeasts from the glucoses of the non-tannins, and (2) the fermentation of the alcohol by acetic bacteria.   In tan liquors it is never formed directly from carbohydrates.

3. Lactic acid is produced by several species of bacteria both from the sugars and other carbohydrates of tan liquors, and from the sugars alone by a yeast.   A good supply of nitrogenous nutriment is necessary for its production, the greater part of which is furnished by the hides.

4. Butyric acid occurs only in *sound* tan liquors.

lead sulphate is removed by filtration through a dried filter and 25 c.c. of the filtrate are taken for the estimation of the sugar. There are mixed in a beaker, 30 c.c. of copper sulphate solution, 30 c.c. of alkaline Rochelle salt solution and 60 c.c. of water. The whole is heated to boiling and the 25 c.c. of extract are added; the beaker is then placed in a boiling water bath for 30 minutes. The cuprous oxide is filtered, dried, heated, and reduced in the usual manner. Should the tanstuff be poor in sugar, or in case the method is applied for the analysis of a leather, which is not weighted with sugar, a larger volume than 25 c.c. may be taken for the estimation, but a correspondingly smaller volume of water must be added to the Fehling's solution, in order that the total volume from which the cuprous oxide is to be precipitated may not exceed 145 c.c.

The quantity of material extracted must vary with its nature, as follows:—

	Grms.
Oak-wood, chestnut-wood, and spent bark	30
Oak-bark, willow-bark, pine-bark, fir-bark, larch-bark, &c.	20
Quebracho-wood, sumac, rove, cayota-bark, garouille, canaigre.	10
Myrobalams, valonia, knoppern	7—10
Mimosa-bark	5—10
Divi-divi, algarobilla, trillo	5

In the examination of extracts, 8–20 grms. of the sample are dissolved in 250 c.c. of this solution, and without filtration, are treated with lead acetate, etc., exactly as described above, the sugar determination being made with 25 c.c., or more, of the final filtrate under the conditions already given. Tanning liquors must generally be concentrated before the precipitation with lead acetate.

In estimating the sugar in a leather it is usual to employ the 20 grms. of the finely-divided sample which have already served for the estimation of moisture, and have been extracted with carbon bisulphide for the estimation of the fat. This portion is extracted in a Koch's apparatus at the ordinary temperature in the manner described above. The litre of extract is concentrated to 500 c.c., and 200 c.c. of this solution serve for the precipitation with lead acetate, etc. Some 40 c.c. of the final filtrate are used for the sugar determination.

The lead acetate solution for this work is prepared by mixing 300 grms. of lead acetate with 100 grms. of litharge and 50 c.c. of water, heating on the water-bath, with replacement of evaporated water, until the mixture is white, digesting with a litre of cold water, and filtering.

	Mean Tannin-Content.	"Sugar"-Content.			Proportion of Acid-yielding Substances to 100 Tannin.
		Mean.	Minimum.	Maximum.	
	Per Cent.	Per Cent.	·Per Cent.	Per Cent.	
Pine-bark extract . . .	25.00	7.84	4.58	9.44	31.4
Pine-bark . . .	11.63	3.53	2.65	4.47	30.4
Oak-bark (young) . .	10.10	2.65	1.75	3.46	26.2
Divi-divi	41.50	8.39	7.98	8.83	20.2
Willow-bark	10.00	2.16	. .	. .	21.60
Canaigre	30.00	6.24	. .	. .	20.80
Algarobilla	43.00	8.23	6.24	10.49	19.1
Myrabolams	30.00	5.35	3.15	7.05	17.8
Sumac (Italian)	28.00	4.53	. .	. .	16.2
Oak-bark extract (Slavonic)	28.00	3.07	2.47	3.92	11.0
Chestnut-wood extract (normal liquid) . . .	30.00	2.87	2.61	3.53	9.6
Valonia	28.80	2.69	1.21	3.57	9.3
Cayota-bark	22.00	1.65	. .	. .	7.5
Hemlock-bark	12.32	0.71	. .	. .	5.76
Trillo from Valonia . .	43.50	2.41	. .	. .	5.5
Garouille	25.00	1.00	0.67	1.51	4.0
Gambier	47.18	1.85	. .	. .	3.92
Rove	29.00	1.13	. .	. .	3.9
Quebracho extract (solid)	70.00	2.41	1.04	3.80	3.4
Mimosa-bark	32.00	0.91	0.33	1.57	2.8
Knoppern	30.00	0.65	0.54	0.71	2.2
Catechu	39.89	0.50	. .	. .	1.25
Quebracho-wood . . .	22.00	0.25	0.10	0.65	1.1

An inspection of the table will show those materials which contain a high ratio of sugar to tannin are those which have always been used for the tanning of such leather as requires an acid liquor for the production of full weight.   It must not be forgotten, however, that although there is direct evidence that the Fehling-reducing compounds give rise to acid, there is not yet evidence that they are the sole cause of acidity; starch under certain conditions can give rise to acids.

Detection of Sumac Adulteration.

Sumac is often adulterated with leaves of *Tamarix africana* and *Pistacia lentiscus*.   In order to detect these adulterations, the following property of a pure sumac decoction is made use of: If lead acetate in caustic potash is added to a decoction of sumac, and the mixture concentrated, a brownish-red liquid is obtained, which assumes a claret color when diluted with water.   The intensity of

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this color will depend on the amount of sumac present, and since the decoctions of the leaves used for adulteration do not give this color, the reaction may be employed not only for their detection, but also for their quantitative estimation by colorimetry. (M. S p i c a, *Gazz. Chim. Ital.*, 1897, 349.)

For this purpose 5 gms. of the sample are boiled for half an hour in half litre of water. After cooling, the liquid is made up to its original volume and filtered. 25 c.c. of the filtrate are run into a flask together with 5 c.c. basic lead acetate (sp. gr. 1.184, containing 250 gms. basic lead acetate per litre) and 15 c.c. caustic potash solution (sp. gr. 1.155). The mixture is shaken and then boiled until the volume has decreased to 15 c.c. In case of pure sumac, the concentrated reddish-brown liquid is almost perfectly clear. The presence of an insoluble precipitate is sufficient to indicate the probability of adulteration. To obtain the amount of adulteration the liquid is diluted to 250 c.c., filtered and examined colorimetrically. The intensity of color of pure sumac is equal to that of a solution of 0.15 gm. of safranine, in 1 litre water, which may be taken as a standard in case a pure sumac sample is unavailable. A suitable colorimeter may be employed for the determination.

Spica also furnishes the following method of determining the presence of *Pistacia lentiscus* in sumac: Half a gramme of the sample is boiled in a test-tube with 5 c.c. of an 18 per cent. solution of caustic potash. Pure sumac gives a brownish-yellow color becoming paler when diluted with water. If *lentiscus* is present the solution assumes a brown color with a violet tint and on dilution this changes to a chestnut brown.

As the ash of *Tamarix africana*, with which sumac is also frequently adulterated, contains considerable sulphuric acid, its presence may be detected in the following manner: 1 gm. of the sample is boiled for half an hour with 100 c.c. water; the filtered liquid is acidulated with nitric acid, and barium chloride is added. If *Tamarix* is present the solution will become turbid.

F. A n d r e a s c h (*Der Gerber*, xxiv, 573) gives the following method for the analysis of sumac containing adulterants from 8 to 60 per cent.: About 20 gms. of the material is treated with a litre of water at 60° C. and filtered. The addition of several drops of formaldehyde (40 per cent. solution) gives a light yellow flocculent precipitate if *Pistacia* is present; care must be taken to have the solution neutral. Arsenious acid solution when warmed with a solu-

tion of *Pistacia*, gives a white precipitate; mercurous nitrate gives a yellow precipitate, which gradually turns green. A pure sumac solution should give no precipitate with formaldehyde. Sulphurous acid and potassium cyanide give no reaction with pure sumac; if *Tamarix* is present, however, sulphurous acid produces a white precipitate or cloudiness; and potassium cyanide gives a dirty-yellow precipitate. Sicilian sumac should never have less than about 22 per cent. of tannin, and not more than 18 per cent. of non-tannins. As the tannin in *Pistacia* and *Tamarix* ranges from 8 to 17 per cent. and the non-tannins from 20 to 26 per cent., a sample of commercial sumac containing less than 20 per cent. of tannin and more than 20 per cent. of non-tannins may be taken as being adulterated.

DYES AND COLORING MATTERS.

Until the middle of this century, nearly all the coloring matters used for dyeing were either such as existed ready-formed in the vegetable or animal kingdom, or were producible from natural products by very simple chemical processes. In a few cases, however, as when chromate of lead or Prussian blue was formed as an insoluble precipitate in the fibre, the dyes were strictly of artificial origin. Now, the vast majority of the coloring matters used as dyes—as distinguished from mere paints or pigments—are products of organic synthesis, being in almost all cases obtained, by a series of highly scientific processes, from c o a l-t a r.

P i c r i c a c i d and a u r i n are the oldest of the coal-tar colors, but the coal-tar color industry may be said to date from 1856, when Perkin accidentally discovered the violet dye called m a u v e, in the course of an investigation having as its object the synthesis of quinine. In 1859 Hofmann synthesized aniline-red (magenta), and in the following year Verguin manufactured it in quantity. In 1860, rosaniline or m a g e n t a first became of commercial importance, owing to the simultaneous discovery of the arsenic acid process by Medlock and Nicholson. P h e n y l a t e d b l u e s were first produced by Girard and De Laire in the same year, but their insolubility rendered their application limited until Nicholson, in 1862, discovered a method of rendering them soluble by conversion into s u l p h o n i c a c i d s. The first azo-dye, amido-azobenzene, was introduced by Simpson, Maule, & Nicholson in 1863, under the name of a n i l i n e y e l l o w, and in the same year the methylated and ethylated rosanilines, known as H o f m a n n ' s v i o l e t s, were manufactured by the same firm. A n i l i n e b l a c k, also, was discovered by Lightfoot in 1863. Azo-diphenyl blue, the first of coloring matters now known as i n d u l i n e s, appeared in 1864, as also did dinitronaphthol or M a n c h e s t e r y e l l o w. In 1866, triamido-azobenzene or B i s m a r c k b r o w n was first made, and in the same year Coupier's n i t r o b e n z e n e p r o c e s s

of manufacturing magenta was introduced. In 1868, Graebe and Liebermann announced their discovery of the constitution of a l i z a r i n, and in the following year this coloring matter was first manufactured from anthracene. G a l l e ï n and f l u o r e s c e ï n were discovered in 1871, and in 1874 tetrabromfluoresceïn was introduced as a dye by Caro, under the name of e o s i n. Diamido-azobenzene or c h r y s o ï d i n e was introduced by Witt in 1875. M e t h y l e n e b l u e and a c i d m a g e n t a were introduced by Caro in 1877, and in the same year the fugitive a n i l i n e y e l l o w was rendered valuable and stable by Grässler, by conversion into a s u l p h o n i c a c i d. In 1878, the t r o p æ o l i n s, f a s t-r e d, n a p h t h o l-s c a r l e t, and other sulphonated azo-colors were first manufactured; and m a l a c h i t e g r e e n dates from the same year. In 1879, the first of the secondary azo-dyes appeared under the name of B i e b r i c h s c a r l e t. The analogous c r o c e i n s c a r l e t s, discovered in 1881, are fast exterminating the cochineal industry. The synthesis of i n d i g o was effected by Baeyer in 1880, and i n d o p h e n o l s were introduced by Koechlin and Witt in 1881. In 1883, Caro's process of manufacturing coloring matters of the rosaniline group by the aid of p h o s g e n e gas was patented. C o n g o-r e d, the first of the numerous class of benzidine dyes, which dye cotton without a mordant, was patented by Böttiger in 1884, and this was followed in the same year by c h r y s a m i n. In 1885, a z o-b l u e and b e n z a z u r i n appeared, and in 1886 the b e n z o p u r p u r i n s were patented. Numerous other dyes are constantly appearing, and in many cases they exceed in fastness, brilliancy, or cheapness those already in the market.[1]

Constitution of Coloring Matters.

The term a n i l i n e d y e is in popular phraseology regarded as synonymous with c o a l-t a r d y e, but this definition is far from accurate. Picric acid and its allies, aurin, the various eosins, alizarin and anthrapurpurin, indigo, and many other important coloring matters are now strictly coal-tar dyes, though they cannot by any straining of the term be appropriately described as aniline dyes.

G r a e b e and L i e b e r m a n n have enunciated the rule that all colored organic compounds (e.g., quinones, azobenzene derivatives, nitro-compounds, etc.) are decolorized by reducing agents, and

[1] See R. Meldola, *Jour. Soc. Arts*, May 26, 1886; or *Jour. Soc. D. & C.* II, 95.

from this they infer that the coloring matters either contain elements with incompletely saturated affinities, or that certain of the atoms are present in more intimate association than their retention in the molecule necessitates. O. W i t t has formulated the conclusion that the tinctorial nature of aromatic compounds is the consequence of the presence together of a color-giving or c h r o m o p h o r i c group, such as NO_2, CO, or N:N, and a s a l t - f o r m i n g group, either OH or NH_2. The common proposition that all bodies containing, for instance, an NO_2 and an OH group are colored, does not hold true. Upon the nature of the salt-forming group depends the character of the coloring matter, those containing OH being usually acids, while all basic coloring matters contain at least one NH_2 group, either intact or substituted.

BASIC COLORING MATTERS, which may be considered as salts of color-bases or phenylated ammonia derivations, are always employed in dyeing in the form of one of their salts, the hydrochloride being the usual form of combination, though the acetate, nitrate, and other compounds are employed in certain cases. Coloring matters of distinctly basic character, which lose their color on coming in contact with acids, cannot be employed in dyeing, except certain very weak bases, which are absorbed by the fibre as such, and not in the form of their salts. Amido-azobenzene (aniline yellow) is an instance of this, for its salts are decomposed by water, and hence, when silk is dyed by an acidulated solution of its hydrochloride, and then washed with water, the free base only remains on the fibre. In the free state, the color-bases are usually colorless, or only slightly colored. Most of them can be converted into soluble acid coloring matters (sulphonic acids) by treatment with strong sulphuric acid.[1]

ACID COLORING MATTERS, like all acids, contain hydrogen which is readily replaceable by metals with formation of salts. The hydrogen may form part of a hydroxyl group, OH, as in picric acid; of a sulphonic group, SO_3H, as in helianthin; of an imido group, NH, as in aurantia; or of a carboxyl group, COOH, as in the scarlet obtained from salicylic acid. Those coloring matters, which owe their acid properties to the hydroxyl group, are very weak acids (e.g., alizarin, aurin); but the acid characters are considerably intensified by the introduction of haloid or nitro-groups. Thus the eosins and nitrophenols have much stronger acid charac-

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[1] Basic aniline colors may be precipitated by soap when the stearates and oleates formed are soluble in benzene. These are known as *resinate* colors.

ters than the fluorescein and phenol from which they are derived. The acid coloring matters (excepting sulphonic acids) are insoluble or only sparingly soluble in water, but dissolve in dilute alkalies. In other words, their alkali-metal salts are soluble, and this solubility increases with the number of hydroxyl groups, but if the hydrogen of the OH be replaced by alkyl radicals, the resultant compounds are rendered less soluble or insoluble in water.   Many of the acid coloring matters unite with metallic hydroxides (e.g., stannic, ferric, chromic, aluminium) to form insoluble compounds called l a k e s.

Sulphonic Acids may be derived from either basic or phenolic colors, and are obtainable either by the action of sulphuric acid on a ready-formed coloring matter, or by the direct transformation of a previously prepared sulphonic acid into a coloring matter.   The sulphonic group, SO_3H, is not a chromophore, and has so little influence on the color that the original and the sulphonated dye are usually of exactly the same color.   The sulphonic acids are usually soluble, and can be employed in acid baths, and volatile coloring matters (e.g., aniline yellow) can be rendered non-volatile by sulphonation.   The salts of the sulphonic acids are generally soluble.   Those derived from azo-dyes have usually the color of the free sulphonic acids, and are taken up by the fibre as salts; while the salts of the sulphonated basic dyes have usually a dull, indefinite color, and in these cases it is the free sulphonic acid which is taken up by the fibre, or rather which is retained by it. Thus, alkali-blue is absorbed by the fibre as a salt, the free sulphonic acid being subsequently liberated by immersion in an acid bath.

Neutral Coloring Matters are rarely met with.   Indigo is the most notable example, but the special means employed in using it sufficiently indicate its exceptional character.

Relations of Coloring Matters to Fibres.

While the chemist defines dyes and coloring matters as acid, basic, and neutral, the dyer classifies them according to their behavior with fibres.   Thus, excluding indigo, aniline black, prussian blue, and a few other coloring matters which are produced by some chemical reaction occurring within the fibre itself, dyes may be classed as s u b s t a n t i v e or d i r e c t, and a d j e c t i v e or m o r d a n t.

Substantive Dyes are absorbed directly from their solutions by

the fibre, and combine with it without requiring the intervention of a mordant. The animal fibres (*e. g.* silk and wool) possess great affinity for most of the coal-tar colors, and in many cases absorb them so completely that the liquid is rendered colorless. Many coloring matters are taken up by animal fibres more readily from an acid than from a neutral bath; and in such cases the bath is usually acidified ("soured") by sulphuric, acetic, or tartaric acid. If sulphuric acid be used, sodium sulphate is generally added also, as the resultant acid sulphate of sodium has less action on the fibre than free sulphuric acid. Some dyers add acid sodium sulphate as such, instead of forming it in the dye-bath.[1] In wool-dyeing, sodium or magnesium sulphate is often added to the bath, to reduce the solubility of the coloring matter, and to obtain faster and more even colors. In order to avoid an uneven or "cloudy" appearance, silk is usually dyed in a weak soap-bath made with Marseilles or good olive-oil soap. If an acid bath is required, boiled-off liquor is used, together with sulphuric or acetic acid.

It is generally assumed that in substantive dyeing a chemical combination ensues between the coloring matter and the fibre. But in some cases, as when wool is dyed with alkali-blue or cotton with indigo, a colorless neutral substance is absorbed by the neutral and indifferent fibre, and is only converted into a colored body by a subsequent chemical reaction, namely, the liberation of the free sulphonic acid in the first case, and oxidization to indigo-blue in the latter.

The "ingrain colors" produced on cotton by means of primuline afford a remarkable example of the building up of a dye within the fibre.

Cotton shows but little tendency to combine with coal-tar dyes, except those known as the b e n z i d i n e or d i a m i n e c o l o r s, which dye it without requiring the agency of a mordant. On the other hand, oxycellulose, vegetable parchment, and the various modifications of nitrocellulose, possess considerable affinity for coal-tar colors.

ADJECTIVE DYEING. MORDANTS.—In many cases, cotton and other vegetable fibres can only be dyed through the intervention of a mordant. Sometimes the mordant acts by forming an insoluble compound with the coloring matter, according to a

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[1] Care must be taken not to employ the impure acid sodium sulphate known in commerce as "nitre-cake," as nitric acid has a very injurious action on many coloring matters.

definite chemical reaction; and in other cases simply serves as a medium on which the color acts as a substantive dye. Albumin acts in this way, as also many substances in a state of fine division, such as calcium phosphate and carbonate, silica, etc., when precipitated on the fibre. In some cases, coloring matters which have themselves been fixed on the fibre act as mordants for others. Thus the benzidine dyes may be employed for mordanting the basic aniline dyes on cotton. Several useful combinations are thus obtainable.

The proteïds resemble silk and wool in their affinity for coal-tar dyes, and hence albumin, etc., are employed in calico-printing. A solution of albumin mixed with the coloring matter is printed on the cotton fibre. On steaming, the ablumin is coagulated and the color becomes fixed.

Tannin acts as a mordant for basic dyes, as it forms with them insoluble tannates.[1] These compounds are soluble in acetic acid or alcohol, and if the solutions thus obtained are thickened with starch or dextrin and printed on cotton, the tannate becomes fixed and insoluble on steaming the goods. Better results are obtained by employing in conjunction with the tannin and color-base a metallic salt (e.g., tartar emetic, stannic chloride, lead acetate, etc.) capable of reacting to form an insoluble tannate.

The use of oil in dyeing turkey-red is a familiar example of the application of oil mordants, which are generally employed in conjunction with inorganic mordants.

Silica, sulphur, and metallic ferrocyanides and sulphides (e.g., of zinc and tin) act as useful mordants for certain dyes.

On soda being added gradually to a solution of lead acetate or aluminium sulphate, avoiding the formation of an actual precipitate, a basic compound is formed which is decomposed by the cotton fibre into a still more basic one which remains fixed and insoluble, and a soluble acid salt. The complete fixation of the mordant can be effected by immersing the cotton in a dilute solution of soap or alkaline carbonate, or by washing it with hard water. Wool has

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[1] The tannates of the color-bases may be either soluble or insoluble, according to the proportions used, the following being the quantities required to form insoluble lakes, according to J. K o e c h l i n : —

Dye.	Tannic Acid.	Soda Crystals.
Magenta 4	5	2
Malachite green, ... 4	5	1
Parma, ... 4	5	1
Methyl green, ... 4	10	4

a greater affinity than cotton for metallic hydroxides, and hence alum is partially decomposed by wool with liberation of sulphuric acid. Chemical equilibrium is soon reached, but if a tartrate be added the absorption of alumina proceeds much further, as tartaric acid is liberated instead of sulphuric acid.

The acetates of iron (ferric), aluminium, and some other metals undergo decomposition when heated, with formation of free acetic acid and insoluble basic acetates. Hence these metallic acetates act as valuable mordants, especially for silk, while they become perfectly fixed on cotton by steaming. The thiocyanates have recently come into use for a similar purpose.

Wool is usually mordanted with chromium or aluminium hydroxides; the former is obtained by the use of bichromate of potash used in conjunction with tartar or sulphuric, oxalic, or lactic acid, or chromium fluoride.

Classification of Dyes and Coloring Matters.

The arrangement of dyes and coloring matters in groups with a view to their convenient description is preferably based on their chemical characters. In certain cases, however, the dyes defy simple classification, and in others a strict adherence to a system produces inconvenience. The coloring matters still obtained from natural sources are also best considered together in the same section, however different they may be in chemical nature.

The following arrangement is that adopted in this work for the description of the dyes and coloring matters and the methods of recognizing them: [1]—

[1] S. de Kostanecki (*Jour. Soc. Dyer's* etc.) has proposed the following scheme for the classification of the organic dyestuffs. He characterizes the formula by the presence of its chromophor which all contain double bonds, and arranges them according to the nature and number of these chromophors:

A. Dyestuffs containing a Single Chromophor.

C : C.	Dibiphenylene ethene.
C : O.	Oxyketones, oxycoumarines, oxyflavones, oxyxanthones.
C : N.	Auramine, thioflavine, quinoline yellow.
$N{\Large\lessgtr}{}^{O.}_{O.}$	Nitro-coloring matters.
N : N.	Azo colors.
N : N : O.	Azoxy colors.

B. Dyestuffs containing Several Chromophors.
(a) Streptostatic Chromophors (Ketone Type).

$\left.\begin{array}{c} C : C \\ C : C \end{array}\right\}$	Unsaturated oxyketones, indogenides, oxyindogenides, indigo.
$\left.\begin{array}{c} C : O \\ C : O \end{array}\right\}$	Oxydiketones, oxydixanthones.
$\left.\begin{array}{c} C : N \\ C : N \end{array}\right\}$	Hydrazone dyestuffs.
$\left.\begin{array}{c} N : N \\ N : N \end{array}\right\}$	Disazo dyestuffs.

1. Nitro-, Nitroso-, and Isonitroso-coloring matters.
2. Azoxy-coloring matters.
3. Hydrazo-derivatives.
4. Azo-, and Tetrazo-coloring matters.
5. Oxyketone derivatives.
6. Di- and Triphenylmethane coloring matters.

(b) *Cyclostatic Chromophors* (*Quinone Type*).

C : C.	C : O.	C : N.
C : O . { Aurins . . . . Benzeins . . . . Phthaleins . . . . } Oxyquinones.		
C : N . { Basic coloring matters of the triphenylmethane group Pyronines . . . . }	Indophenols. Nitrosophenols.	{ Indamines. Azines. Safranines. Indulines.
C : N : O	Resazurine.	

(c) *Streptostatic and Cyclostatic Chromophors.*

This group comprises several complicated coloring matters, such as Alizarin Blue, Styrogallol, &c.

W. S c h a p o s c h i n k o ff (*Chem. Zeit.*, xxii. 55) has also proposed a classification which is intended to express both the chemical character of the dyestuff and its relation to the fibre, as well as the method of its application.

I. Dyestuffs with Acid Characteristics.		II. Dyestuffs with Salt-like Characteristics. Substantive Dyestuffs.	III. Dyestuffs with Basic Characteristics.	IV. Indifferent Dyestuffs.	
Group 1.	*Group* 2.	*Group* 3.	*Group* 4.	*Group* 5.	*Group* 6.
Dyestuffs Dyeing from an Acid Bath.	Dyestuffs which Dye on Metallic Mordants.	Dyestuffs which Dye from a Neutral or Alkaline Bath.	Dyestuffs which Dye from a Neutral Bath	Dyestuffs which are formed on the Fibre.	Dyestuffs mechanic-ally attached to the Fibre.
1. Nitro - dye-stuffs. 2. Most of the a z o - d y e-stuffs. 3. Triphenyl-me t h a n e sulphonic acids, in-duline and q u i noline d y e stuffs, indigo car-mine. 4. Hydrazone dyestuffs. 5. C h r o m o-trope.	6. Some a z o-dyestuffs. 7. Oxyquinone and quinone oxime dye-stuffs. 8. Some quin-o n e-i m i d e dyestuffs. 9. Oxyketone, x a n t h o n e, and flavone dyestuffs. 10. P h t h alein and rosolic a c i d d y e-stuffs. 11. N a t u r a l dyestuffs.	12. Some nat-u r a l d y e-stuffs. 13. T e t r a z o dyestuffs. 14. T h i a z o l dyestuffs.	15. Basic azo-dyestuffs. 16. D i- a n d tri-phenyl-me t h a n e dyestuffs. 17. M o s t of the q u i n-o n e-i m i d e dyestufts. 18. Q u i n o-line a n d a c r i d i n e dyestuffs.	19. Metals. 20. I n s o l u b l e azo-dyestuffs. 21. M i n e r a l colors. 22. Indigo and indophenol. 23. A n i l i n e black. 24. C a t e c h u, bistre, cana-rin.	25. Albumin colors.

1. Nitro-, Nitroso-, and Isonitroso-coloring Matters.

Of this class, the nitro-coloring matters are the most numerous and also the most important; the other two groups of this class yield but a few unimportant dyestuffs.

(a.) Nitro-bodies.

Nitric acid acts very violently on phenol and similar bodies, and by the direct reaction or by indirect means a number of bodies may be obtained, some of which are coloring matters of considerable commercial importance.

The resulting nitro-compounds contain one or more atoms of the radical n i t r y l, (NO_2), in place of the hydrogen of the original substance. They are crystalline bodies, usually more or less yellow in color, only slightly soluble in cold water, and not soluble to any great extent in boiling water; but they are readily soluble in alcohol and ether, and are removed by the latter solvent from their acidulated aqueous solutions.

The n i t r o p h e n o l s and their allies have marked acid properties, readily decomposing metallic carbonates, and furnishing a series of salts all or nearly all of which are more or less soluble in water, and often form crystals of great beauty, ranging in color from a pale yellow to a fine crimson. The salts of the nitro-phenols and their allies all deflagrate with greater or less facility when ignited, and many of them detonate on percussion, the more highly nitrated compounds (e. g., the picrates) exploding with considerable violence.

In cases where the nitro-body is the product of a limited nitration, it may be converted into the corresponding s u l p h o n i c a c i d by treatment with strong sulphuric acid; but this is not possible when, as in the case of picric acid, the number of nitro groups in the molecule is at the maximum. With the exception of flavaurin, naphthol yellow S, and Schoellkopf's brilliant

yellow, none of these dyestuffs are sulphonated compounds. The sulphonic acids of the nitro-coloring matters are stable bodies, readily soluble in water. The nitro-coloring matters as a class dye wool and silk yellow or orange, but have no affinity for cotton. Their acid characters are well marked and stronger than the phenoloïd bodies from which they are derived.[1] They dissolve in concentrated sulphuric acid to form yellow or colorless solutions. Strong reducing agents, such as stannous chloride and hydrochloric acid, convert them into the colorless a m i d o - d e r i v a t i v e s. Fibres dyed with nitro-coloring matters, or aqueous solutions of the bodies themselves, are but slightly altered by hydrochloric acid, while ammonia and caustic soda tend to darken or redden the color. With fibres dyed by nitro-coloring matters in acid baths, the color may subsequently be partly removed by boiling water. These reactions serve to distinguish the nitro-dyes from other yellow coloring matters. Thus p h o s p h i n e is turned light by ammonia, while the yellow a z o - d y e s are reddened by acids. Phosphine, again, is extracted from its alkaline aqueous solutions on agitation with ether, but the nitro-compounds are not dissolved by ether under similar conditions. In presence of dilute sulphuric acid in excess, the simple nitro-dyes (e. g., picric acid, dinitrocresol, dinitronaphthol, and aurantia) are extracted by ether, but the sulphonic acids (e. g., naphthol yellow S) are not dissolved, in this respect resembling the yellow azo-dyes (except chrysamin).

The nitro-colors are sold in the form of their alkali or lime salts; picric acid, however, is an exception, it being sold in the free state owing to the explosive nature of the picrates.

The nitro-dyestuffs produce yellow to orange yellow colors when dyed on the animal fibres; but they have no practical application in cotton dyeing. As a class their use is gradually decreasing, although the naphthol yellows and brilliant yellow still appear to maintain their prestige in the trade.

[1] Nitro-derivatives in general appear to possess more or less tinctorial properties, and especially those of the amines and phenols; but it is only in derivatives of the latter that the coloring power assumes the pronounced character of a dyestuff. In amine derivatives, the basic properties of the amido-group decrease with the number of nitro-groups introduced into the molecule ; in fact, in a body like diphenylamine, where the basic character is but feeble, the introduction of several nitro-groups will give rise to an acid dyestuff. The salts of the acid nitro-derivatives have a more pronounced color than the free acid itself; for instance, paranitrophenol is a colorless substance, whereas its salts have a pronounced yellow color.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Picric Acid.	$C_6H_2 \begin{cases} (1)OH \\ (2)NO_2 \\ (4)NO_2 \\ (6)NO_2 \end{cases}$	Action of nitric acid on phenol.
Victoria Yellow.	$C_6H_2 \begin{cases} (1)OK \\ (2)CH_3 \\ (3,5)(NO_2)_2 \end{cases}$ and $C_6H_2 \begin{cases} (1)OK \\ (4)CH_3 \\ (3,5)(NO_2)_2 \end{cases}$	From ortho- and para-cresol.
Naphthol Yellow.	$(Acid)$ $\quad C_{10}H_5 \begin{cases} (1)OH \\ (2)NO_2 \\ (4)NO_2 \end{cases}$	From alpha-naphthol.
Naphthol Yellow S.	$C_{10}H_4 \begin{cases} (1)OK \\ (2)NO_2 \\ (4)NO_2 \\ (7)SO_3K \end{cases}$	From alpha-naphthol.
Brilliant Yellow.	$C_{10}H_4 \begin{cases} (1)OH \\ (2)NO_2 \\ (4)NO_2 \\ (8)SO_3Na \end{cases}$	From acid Sch.
Aurantia.	$N(NH_4) \begin{cases} (2)C_6H_2 \begin{cases} (1)NO_2 \\ (3)NO_2 \\ (5)NO_2 \end{cases} \\ (2)C_6H_2 \begin{cases} (1)NO_2 \\ (3)NO_2 \\ (5)NO_2 \end{cases} \end{cases}$	From diphenyl-amine.
Nitrosamine Red.	$C_6H_4 \begin{cases} (1)N<^{NO}_{Na} \\ (4)NO_2 \end{cases}$ or $C_6H_4 \begin{cases} (1)N=N.ONa \\ (4)NO_2 \end{cases}$	
Mikado Golden Yellow 2 G, 4 G, 6 G, 8G. Direct Yellow 2 G, 3 G.	$CH(1)C_6H_3 \begin{cases} (4)NO_2 \\ (6)SO_3Na \end{cases}$ $\overset{\|}{C}H(1)C_6H_3 \begin{cases} (4)NO_2 \\ (6)SO_3Na \end{cases}$	
Flavaurin. New Yellow.	$C_6H_2 \begin{cases} (1)ONH_4 \\ (2)NO_2 \\ (4)SO_3NH_4 \\ (6)NO_2 \end{cases}$	
Salicyl Yellow A.	$C_6H_2.Br.(NO_2) \begin{cases} (1)CO_2H \\ (2)OH \end{cases}$	From salicylic acid.
Salicyl Orange.	$C_6HBr(NO_2)_2 \begin{cases} (1)CO_2Na \\ (2)ONa \end{cases}$	From salicylic acid.
Palatine Orange.	$C_6H_2 \begin{cases} (NO_2)_2 \\ (4)ONH_4 \end{cases}$ $\overset{|}{C}_6H_2 \begin{cases} (4)ONH_4 \\ (NO_2)_2 \end{cases}$	From tetrazo-diphenyl.
Sun Gold. Heliochrysin.	$C_{10}H_3 \begin{cases} (1)ONa \\ (NO_2)_4 \end{cases}$	
Citronin.	$NH \begin{cases} C_6H_3(NO_2)_2 \\ C_6H_3(NO_2)_2 \end{cases}$ and $NH \begin{cases} C_6H_4.NO_2 \\ C_6H_4.NO_2 \end{cases}$	From diphenyl-amine.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Yellow crystals; Yellow solution.					Soluble in alcohol. With KCN— brown sol.
Orange powder; Orange solution.	No change.	White pp.	Pale yellow.		Used for coloring foods.
Orange yellow plates; Yellow solution.		Precipitates dinitronaphthol.			Soluble in alcohol.
Orange yellow powder; Yellow solution.	Yellow pp.	Yellower.			
Yellow powder; Yellow solution.	Orange pp.	Clear yellow solution.	Pale Yellow.		
Brown crystals; Orange solution.		Yellow pp.			
Yellow paste; Yellow solution.		Yellow pp.			
Yellow powder; Yellow solution.	Yellow pp.	Browner.	Red.	Yellow.	
Orange powder, Yellow solution.	Darker.	Claret red.	Claret red.	Colorless.	Obsolete.
Pale yellow powder; Yellow solution.					Obsolete.
Orange powder; Orange solution.	No change	White pp.			Obsolete. Soluble in alcohol.
Brown powder; Orange solution.		Brown pp.			Obsolete.
Orange scales; Orange solution.		Yellow pp.			Obsolete.
Orange lumps containing soap; Orange solution.	Yellow pp.	White emulsion.	Brown.	Yellow.	Obsolete.

The following sections contain detailed descriptions of the principal nitro-coloring matters.

Picric Acid.   Para-diortho-trinitrophenol.   Trinitrophenic Acid. $C_6H_3N_3O_7 = C_6H_2 \begin{cases} OH \\ (NO_2)_3 \end{cases}$.

This substance, formerly called c a r b a z o t i c a c i d, is the final product of the action of nitric acid on a large number of substances containing a benzene nucleus, just as oxalic acid is the result of the oxidation of many bodies of the fatty series.   Picric acid is obtainable from indigo, aloes, gum-resins, wool, silk, &c.[1]

Picric acid was formerly prepared by the direct action of nitric acid on phenol, but is now made by first dissolving the phenol in strong sulphuric acid and then acting on the resultant phenol-sulphonic acid with excess of nitric acid.[2]   Mono- or dinitro- phenol may result if the action is not carried sufficiently far.[3]   According

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[1] The common idea that the yellow color produced by nitric acid on animal tissues, such as skin, wool, etc., is due to the production of picric acid, is erroneous; it is due to the formation of xanthoproteic acid.

[2] Picric acid is now manufactured on a large scale by mixing equal parts by weight of crystallized carbolic acid and concentrated sulphuric acid.   This is heated to 100° until a sample is found to be completely soluble in water, when a double equivalent of nitric acid of 1.3 sp. gr. is allowed to flow in, the whole being continually agitated.   In some works, the phenol-sulphonic acid, slightly diluted, is run into strong nitric acid. On cooling, the product forms a crystalline mass, which is filtered off, drained, and washed with cold water.   It is then purified by crystallization from boiling water containing 0.1 per cent. of sulphuric acid; or the hot solution of the crude acid is exactly neutralized with sodium carbonate, the liquid filtered to separate resin, and excess of sodium carbonate added to the filtrate, when almost the whole of the sodium picrate separates.   This salt is decomposed by sulphuric or hydrochloric acid and the picric acid crystallized.   Sodium sulphate is sometimes added before crystallization, as an adulterant.

[3] The first product of the action of nitric acid on phenol is a mixture of p a r a- m o n o n i t r o p h e n o l, $C_6H_4(NO_2).OH$, with the isomeric o r t h o-d e r i v a t i v e. These bodies are best obtained by adding sufficient water to pure phenol to prevent it from solidifying on cooling, and then adding the resultant hydrous phenol drop by drop to a well-cooled mixture of two parts of nitric acid of 1.34 sp. gr. and four parts of water.   A heavy bromine-like oil separates, and on prolonged standing sets to a crystalline mass.   This consists of a mixture of ortho- and para-nitrophenol, with some unaltered phenol.   The higher the temperature has been allowed to rise the larger the proportion of the ortho-modification formed.   The product is washed with cold water, and then distilled in a current of steam, when the ortho-nitrophenol dissolves over, and may thus be separated from the para-modification, which is not volatile, and may be obtained from the contents of the distilling flask by cooling and recrystallizing from boiling water.

A meta-mononitrophenol is obtainable from meta-nitraniline by the action of nitrous acid.

to T. W h i t a k e r (*Jour. Soc. Dyers, &c.*, iv. 87), if the sulphuric acid used for sulphonation contain nitrous compounds the picric acid has a brownish color instead of being pure yellow.

On warming the ortho-mononitrophenol with nitric acid of 1.36 sp. gr., violent action ensues and another nitro-group is assimilated, a product being obtained which is chiefly a mixture of d i o r t h o-d i n i t r o p h e n o l and o r t h o-p a r a-d i n i t r o p h e n o l, $C_6H_3(NO_2)_2$.OH. The product is washed with cold water, and then boiled with water in a flask through which a current of steam is passed, to remove unaltered mononitrophenol. It is then boiled with water and excess of barium carbonate, and the solution filtered. On cooling to 40°, the barium salt of diortho-dinitrophenol crystallizes out, while the corresponding salts of ortho-para-dinitrophenol and picric acid remain in solution. A better separation of the barium salts of the isomeric dinitrophenols can be obtained by rectified spirit, in which the ortho-para-salt dissolves with moderate ease, while the diortho-compound is nearly insoluble. S a l k o w s k i converts the mixed barium salts into potassium salts by potassium carbonate, and removes the greater part of the ortho-para-salt by crystallization; then heats the mother-liquor to 40°–50° C. and precipitates with barium chloride, which throws down the diortho-compound. This is washed with cold water and purified by recrystallization. From their salts the dinitrophenols may be obtained free by adding excess of dilute sulphuric acid and agitating with ether. The ethereal layer leaves the nitrophenol on evaporation.

By the action of boiling concentrated nitric acid the meta-dinitrophenols are converted into t r i n i t r o r e s o r c i n o l or s t y p h n i c a c i d, $C_6H(NO_2)_3.(OH)_2$.

The following table summarizes the properties of the nitrophenols at present known:—

Formula.	Name.	Position of the NO_2 group, OH being 1.	Melting point ° C.	Characteristics.
$C_6H_4(NO_2)$.OH.	Para-mononitro-phenol.	4	114	White prisms; not volatile in a current of steam.
Do.	Meta-mononitro-phenol.	3	96	Almost colorless prisms or feathery plates; not volatile with steam.
Do.	Ortho-mononitro-trophenol.	2	45	Pale yellow prisms; readily volatile with steam.
$C_6H_3(NO_2)_2$.OH.	a–or Para-ortho-dinitrophenol.	2 : 4	114	Striated, yellowish-white plates united in fern-like forms.
Do.	β–or Diortho-dini-trophenol.	2 : 6	64	Slender, short, bright yellow needles.
Do.	γ–Dinitrophenol.	3 : 6	104	Slender, short, pale yellow needles; volatile with steam.
Do.	δ–Dinitrophenol.	3 : 4	134	Long, colorless, silky needles; not volatile with steam.
Do.	ϵ–Dinitrophenol.	2 : 3	144	Small yellow needles.
$C_6H_2(NO_2)_3$.OH.	a–or Para-diortho-trinitrophenol (picric acid).	2 : 4 : 6	122	Pale yellow laminæ or prisms; not volatile with steam.
Do.	β–Trinitrophenol. (from meta-nitro-phenol).	3 : 4 : 6	96	White satiny needles or scales.
Do.	γ–Trinitrophenol.	2 : 3 : 6	117	White needles.

Picric acid may also be prepared by acting on phenol-trisulphonic acid with sodium nitrate.

Picric acid forms pale yellow, crystalline needles or scales, of an intensely bitter taste and 1.777 specific gravity. The pure acid melts at 122° C. and the common at a lower temperature, to a brownish-yellow oil, which at a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapors. The lower melting point of impure picric acid is probably due to an admixture of dinitrophenols or of a nitrocresol. Hence the melting point of picric acid is a test of its purity.

When strongly heated, picric acid burns rapidly with formation of an intensely black smoke. It is commonly stated to be liable to explode when strongly heated, but this is doubtful, and is opposed to the direct experiments of Dupré and Abel. On the other hand, picric acid can be detonated by a blow, a charge of 5 grains of fulminate of mercury sufficing to determine the explosion. The detonation of one charge will cause the detonation of neighboring quantities, and even wet picric acid can be exploded by this means. Metallic picrates, and notably picrate of lead, or even an imperfect mixture of picric acid with oxide or nitrate of lead, will detonate violently when heated, and the explosion will induce the detonation of neighboring quantities of picric acid or picrates. This property of the picrates has led to their employment in several detonating and explosive mixtures [1] (see page 116).

Picric acid is soluble in about 15 parts of boiling water, but it requires 26 parts at 76° and 86 at 15° C. The solution is intensely bitter, bright yellow, and reddens litmus. In a stratum one inch in depth, the yellow color of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow color of picric acid solutions is intensified by neutralization with an alkali. A cold aqueous solution of picric acid gives a copious precipitate on adding hydrochloric acid.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, etc.; the last four solutions being colorless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidulated with sulphuric acid. Ether is preferable to chloroform for this purpose. A solution of picric acid in ether gives up the greater part of its

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[1] Several disastrous fires and explosions have occurred through the negligent handling and storage of picric acid.

color to water, but on adding sulphuric acid, or still better, hydrochloric acid, the condition is reversed, the picric acid going chiefly into the ether.

All the above solutions of picric acid, including the aqueous, dye silk, wool, skin, and other nitrogenous organic matters a yellow color of a slightly greenish shade.[1] The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution.[2]

Picric acid forms a series of well-defined crystallizable metallic salts and also combines with organic bases. With certain hydrocarbons it forms characteristic crystalline compounds of the formula $X,C_6H_2(NO_2)_3O$, in which X represents a molecule of the hydrocarbon. The reaction has been utilized for the purpose of distinguishing hydrocarbons, especially those of the anthracene group, and the formation of the naphthalene and acridine picrates has been suggested as a means of identifying picric acid.

DETECTION AND DETERMINATION OF PICRIC ACID.—The yellow color and extremely bitter taste of the aqueous solution of picric acid, the deepening of the yellow color on adding excess of alkali, and the power possessed by the solution of the free acid of dyeing immersed wool or silk yellow, are themselves important indications of its presence. In the presence of other coloring or interfering bodies,[3] the picric acid may be extracted from the aqueous solution by agitation with ether or amylic alcohol, after strongly acidulating with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution, or agitating it with solution of caustic soda, when it will pass into the alkaline liquid. The extraction of picric acid from an acidulated solution by ether, benzene, or amylic alcohol may be made quantitative.

Picric acid may be titrated with ease and accuracy by standard caustic alkali and phenol-phthalein (P. K a y, *Jour. Soc. Dyers, &c.*, iv. 84). The process is applicable to the ethereal or benzene solution of picric acid if this be first diluted with alcohol.

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[1] Picric acid is used as a dye for silk and wool, but is employed to modify the shades of other colors rather than as an unmixed dye. Thus with methyl-green it gives a yellow-green, with indigo-carmine or aniline-blue a deep green, and with magenta a very fast scarlet. Since the introduction of the yellow azo-dyes the employment of picric acid has decreased.

[2] Picric acid has been used in Eczema; and it has also been found useful in the treatment of burns.

[3] The dyestuff E c h u r i n is a mixture of picric acid and nitro-flavin.

An aqueous solution of picric acid is not precipitated on adding neutral lead acetate, but basic or ammoniacal lead acetate gives a bright yellow precipitate even with very dilute solutions of picric acid.[1]

Picric acid is not precipitated from its aqueous solution by cupric sulphate; but the ammonio-sulphate produces a bright green precipitate, which is insoluble in ammonia, and is decomposed by washing with water. A solution containing 1–10,000 of picric acid gives a distinct precipitate with ammonio-sulphate of copper in twenty-four hours.

If a solution of picric acid be treated with zinc and dilute sulphuric acid, a turbid yellowish-red solution is obtained, which, when poured off from the excess of zinc and mixed with alcohol, develops a green color, changing through blue to a violet.

By the action of tin and hydrochloric acid in a warm solution, picric acid is completely reduced to the colorless hydrochloride of t r i a m i d o - p h e n o l, $C_6H_2(NH_2)_3.OH$. In alkaline solutions, the reduction does not proceed so far, p i c r a m i c a c i d, $C_6H_2(NO_2)_2(NH_2).OH$, being the product. This reaction occurs most readily by passing sulphuretted hydrogen through a saturated alcoholic solution of picric acid neutralized with ammonia. Dark red crystals of ammonium picramate are deposited, from which the free acid may be prepared by dissolving in hot water and adding acetic acid. Picramic acid forms beautiful red needles, almost insoluble in water even when hot, but soluble in alcohol and ether. It dyes silk and wool brown.[2]

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[1] If the precipitate be decomposed by dilute sulphuric acid, and the filtered solution rendered ammoniacal and evaporated to dryness, a residue is obtained which gives a deep brown color on heating with potassium cyanide. This behavior distinguishes picric acid from quercitron and such other vegetable yellow coloring matters as are precipitated by basic lead acetate.

[2] E. T u r p i n has patented (No. 10,665, 1887) the use, as a substitute for gunpowder, of the product resulting from the reduction of picric acid by boiling its aqueous solution with metallic zinc or iron. When acetic acid is also added, picramic acid is formed, and this, or its sodium salt, in admixture with nitre, yields a powerful detonating explosive. Mixtures containing from 30 to 50 per cent. of picramic acid, or 25 to 53 of sodium picramate, are recommended.

The nature of the French explosive *mélinite* has not been made public, but its composition is not improbably indicated by that of the foregoing mixtures; or perhaps has a connection with another patent of the same inventor (No. 10,667, 1887), who has proposed the use, as explosives, of chloro-picrin, bromo- chloro- and iodo-dinitrophenols, bromo-dinitrobenzene, chloro-trinitrobenzene, and tetra-nitro-chloronaphthalene.

When a solution of picric acid is boiled with a strong solution of potassium cyanide, a deep red liquid is produced,[1] owing to the formation of p o t a s s i u m i s o-p u r p u r a t e, a body which crystallizes in small reddish-brown plates with a beetle-green lustre, and is slightly soluble in cold but more readily in hot water. By reaction with ammonium chloride, it gives a m m o n i u m i s o-p u r p u r a t e, $NH_4,C_8H_4N_5O_6$, or artificial *murexide*, which in a slightly acid bath dyes silk and wool a beautiful brown-red color. It was formerly employed under the name of "grenat soluble," but is not now used. On adding barium chloride to a solution of either of the above salts a vermilion-red precipitate is formed, consisting of b a r i u m i s o - p u r p u r a t e. True iso-purpuric acid is very unstable and is practically unknown.

Picric acid, when boiled with a strong solution of calcium hypochlorite (bleaching powder), gives off pungent and tear-exciting vapors of c h l o r o p i c r i n, $C_6H_2(NO_2)Cl_3$.

Picric acid forms highly insoluble compounds with many of the vegetable alkaloids,[2] and the insolubility of the cinchonine salt has been employed for the determination of picric acid. A solution of cinchonine sulphate acidulated with sulphuric acid is added to the picric acid solution. The precipitate of p i c r a t e o f c i n c h o n - i n e, $C_{20}H_{24}N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. The yellow, intensely bitter alkaloid, b e r b e r i n e, is said to precipitate picric acid so perfectly that, on mixing the picric and alkaloidal solutions in equivalent proportions and filtering, the filtrate is colorless and perfectly free from bitter taste.

Some of the color-bases from coal-tar form extremely insoluble picrates, and have been employed by K a y and A p p l e y a r d (*Jour. Soc. Dyers*, &c., iv. 83) for the determination of picric acid. For this purpose they prefer the dye known as n i g h t - b l u e, which is the hydrochloride of tetramethyltolyltriamido-diphenyl-naphthyl-carbinol. The commercial product is purified by precip-

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[1] Aniline yellow of commerce dissolves in water with redder color than picric acid. It is not altered by potassium cyanide, but is turned purple by hydrochloric acid.

[2] The cinchona alkaloids, the opium bases (except morphine and pseudo-morphine), the *strychnos* alkaloids, veratrine, berberine, and some others, are completely precipitated by picric acid from their dilute solutions, if acidulated by sulphuric acid, but not in presence of free hydrochloric acid. Caffeine and the glucosides are not precipitated by picric acid.

itating the aqueous solution with ammonia, washing well with water, and drying the precipitate over strong sulphuric acid. A weighed quantity of the base is dissolved in acetic acid and the solution diluted to a known volume. For the titration, a known volume of the night-blue solution is measured into a flask, and the solution of picric acid run in from a burette. 485 parts of the night-blue base correspond to 229 of picric acid, the picrate, which forms a dark precipitate, having the formula $C_{34}H_{36}N_3.C_6H_2(NO_2)_3OH$. The picric acid solution should contain 1 gramme of the sample per litre, and by comparing the volume of the solution used with the measure of a solution of pure picric acid employed in a parallel experiment, the proportion of impurity may be readily ascertained. The end of the reaction is very sharply defined, as by tilting the flask on one side, so that a portion of the clear liquid may run into the neck, it is easy to observe whether the solution retains any blue color. A very slight excess of picric acid is sufficient to produce a marked yellow tint. If desired, a portion of the liquid may be filtered for the better observation of its color, but this is rarely necessary.

C r y s t a l v i o l e t, the hydrochloride of hexamethyl-rosaniline, may be substituted for the night-blue in the above process. 443.5 parts of this coloring matter, when dissolved in water, react with 229 parts of pure picric acid to form a picrate of the formula $C_{25}H_{31}N_3.C_6H_2(NO_2)_3OH$. This precipitate is flocculent, and when in suspension exhibits such a powerful coppery reflex that the liquid containing it appears brown by reflected light.

The picrates of rosaniline, safranine, methyl-violet, methylene-blue, and malachite-green, are also nearly insoluble in water, but not sufficiently so to render the bases desirable substitutes for night-blue or crystal-violet in the above process.

Of the compounds of picric acid with solid hydrocarbons, that with n a p h t h a l e n e, $C_{10}H_8 + C_6H_3(NO_2)_3O$, is almost the only one precipitated when the cold alcohol solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149° C. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitro-compounds.

Acridine has been suggested by A n s c h ü t z (*Jour. Soc. Chem. Ind.*, iii. 234) as a suitable reagent for the determination of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons.

Picric acid has been used occasionally to communicate a bitter taste to *beer*, less than 1 grain per gallon being amply sufficient for this purpose. The employment of picric acid as a "hop-substitute" is objectionable, as it has distinct poisonous properties, and rabbits and dogs have been killed by doses varying from 0.06 to 0.60 gramme. The most delicate and satisfactory method for the detection of picric acid in beer is to concentrate 100 c.c. by evaporation to about 30 c.c.; then acidulate with sulphuric acid and agitate with ether or petroleum spirit. The ethereal solution is separated and evaporated. The residue is dissolved in hot water and the solution heated on the water-bath for some time with a small quantity of white Berlin wool, which in presence of picric acid will acquire a yellow color. The author has readily detected 1 part of picric acid in 100,000 of beer by this method. Amylic alcohol has been proposed as a substitute for ether, but, in the opinion of the author, is not so satisfactory. By first precipitating the beer with neutral acetate of lead and filtering, the coloring matter of the beer may be removed and the indications made more delicate. As a confirmation, the dye may be removed from the wool by warming it with dilute ammonia, filtering, and evaporating the filtrate to a very small bulk on the water-bath. On then adding a few drops of potassium cyanide solution, and heating, a distinct red-brown color will be produced in presence of picric acid;[1] or the ammoniacal extract may be treated with zinc and hydrochloric acid and the solution diluted with alcohol, as described on page 116.

It is evident that the method just described is applicable to the detection of picric acid on animal fibres, such as *silk* or *wool*.

COMMERCIAL PICRIC ACID.

The picric acid of commerce is generally crystallized. Though now of much better quality than formerly, it is still liable to contain impurities, and occasionally is intentionally adulterated. Thus sodium sulphate is sometimes added before crystallization, and oxalic acid and sugar are said to be occasionally met with.

The m e l t i n g p o i n t of pure picric acid is 122° C., and the best commercial samples do not melt below 121°. A lower melting point indicates the presence of *dinitrophenol* or a *nitrocresol*. The first impurity is due to imperfect nitrification and the latter to the employment of a picric acid of low melting point (there-

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[1] A rough colorimetric determination of the amount of picric acid present may be based on the depth of color produced.

fore containing cresol) for the manufacture. The melting point of picric acid is best observed by placing a minute fragment of the sample on the surface of some clean mercury contained in a porcelain crucible or small beaker. The latter is covered with an inverted funnel or bottomless flask, through the neck of which a thermometer passes and is held by a perforated cork in such a position that the bulb may be entirely immersed in the mercury, without touching the side or bottom of the beaker or crucible. The latter is now heated on an iron plate, and the temperature at which the fragment of picric acid liquefies recorded as the melting point. By employing several fragments and repeating the experiment after allowing the mercury to cool a few degrees, very fairly concordant results are obtainable.

More rapid, and for technical purposes quite as satisfactory, results are obtainable by determining the s o l i d i f y i n g p o i n t of the sample. This is effected by melting 8 or 10 grammes of the picric acid in a small test-tube, which is then fixed by means of a perforated cork in the mouth of an empty, short-necked flask. The melted picric acid is continually stirred with a thermometer, while the temperature is carefully watched. At a certain point the mercury ceases to fall, remaining stationary for fully half a minute, or even rising again slightly. This temperature, which is perfectly definite, is recorded as the solidifying point of the sample.

The following figures, obtained in the author's laboratory by the examination of six samples of commercial picric acid, show the constancy of the results yielded. It will be observed that, while the solidifying point is always several degrees lower than the melting point of the same sample, the difference between the two results is not a constant figure:—

Sample.	Melting Point ° C.	Solidifying Point ° C.	
		Observations.	Mean.
A	122, 122	115, 115, 115.5, 115, 115.	115.1
B	118, 118	114, 113, 112, 113, 113.5, 113, 113.	113.1
C	121, 121	115.5, 116, 115.	115.5
D	120, 119	114.5, 114.5.	114.5
E	117.5, 117.5	113.5, 112.5.	113.0
F	122, 122	117, 117, 118, 118, 118, 117, 118, 118, 118.	117.7

Picric acid of good quality does not melt when boiled with twice its weight of water. If fusion occur, it is probably due to the presence of nitrocresols, which for some purposes are objectionable.

The best commercial picric acid is completely soluble in 15 times its weight of boiling water, or leaves only a trifling quantity (0.5 per cent.) of *granular* impurity. Picric acid of inferior quality leaves a *melted globule* when similarly treated. The scientific advisers of the French Government call this insoluble matter "dinitrophenol" (!), apparently without any evidence of its nature, and reject, as unsuited for the manufacture of mélinite, all picric acid which leaves a globule amounting to more than 1 per cent. of the sample. The test is made by treating 10 grammes of the acid with 150 c.c. of water, and heating the liquid to boiling in a flask with gentle agitation, till the globule of insoluble matter becomes transparent and ceases to diminish perceptibly in bulk. This point is reached in about ten minutes from the commencement of ebullition. The test must not be much prolonged, or the so-called "insoluble matter" will partly dissolve. The critical point is by no means well defined, though with care and experience fairly concordant results are obtainable with some samples, while others behave very erratically. When the operation is considered to be complete, the liquid is allowed to cool slightly and poured off from the globule of "dinitrophenol," which is then washed with cold water, dried by means of filter-paper, and weighed.

Any *resinous matters* will also be left insoluble on dissolving commercial picric acid in boiling water. The separation will be more perfect if the hot solution be exactly neutralized with caustic soda.

Besides being soluble in 15 parts of boiling water, picric acid of good quality dissolves completely in 10 parts of alcohol, while any metallic *sulphates* or *nitrates* will be left insoluble.

General impurities and adulterations may be detected and determined by treating 2 grammes of the finely-powdered sample with 50 c.c. of ether. The picric acid dissolves, while any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, etc., will be left insoluble, and, after removal of the ethereal liquid, may be readily identified and determined. For the detection and determination of *water* and *oxalic acid*, 50 c.c. of warm benzene may be advantageously substituted for the ether. Sugar and boric acid may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified

spirit. If *boric acid* be present the alcoholic solution will burn with a green flame. *Sugar* may also be sought for by neutralizing the aqueous solution of the sample by sodium carbonate, evaporating to dryness, and extracting with proof-spirit, which will dissolve any sugar and leave the sodium picrate insoluble.

Sulphuric, hydrochloric, and oxalic acids, and their salts, may be detected by adding solutions of barium, silver, and calcium, respectively, to the warm, filtered, aqueous solution of the sample. 0.2 per cent. of SO_3, as estimated by precipitation as barium sulphate, is the maximum proportion allowed by the French Government in picric acid intended for the manufacture of mélinite. *Free sulphuric acid* might be detected by dissolving the sample in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene, till all yellow color is removed. On then titrating the aqueous liquid with standard alkali, the volume required for neutralization will correspond to the free sulphuric or other mineral acid of the sample.

It is possible that commercial picric acid occasionally contains a *nitrophenol-sulphonic acid.* Such an impurity would be indicated by the presence of sulphates in the residue obtained on igniting the sample after neutralization with a fixed alkali. The explosive character of the picrates prevents the direct application of this method, but ignition of the picric acid in admixture with a large excess of lime or magnesia would probably answer, or the sample might be dissolved in alcohol together with some ammonium carbonate, and the alcohol burnt in a lamp connected with an apparatus similar to that employed for determining the proportion of sulphur in coal-gas. (See *Analyst*, xiii. 43.)

If the process of nitrification has been imperfect, the resultant picric acid will be liable to contain *dinitrophenol* (see above). This impurity lowers the melting point of the sample. The calcium salt is less soluble than calcium picrate, and if present in sufficient quantity may be separated from the latter by fractional crystallization, or by precipitating the hot saturated aqueous solution of the sample with excess of lime-water.

The most promising, if not the only method of determining small proportions of dinitrophenol in picric acid is by treating the aqueous solution of the sample with bromine, as proposed by the a u t h o r (*Jour. Soc. Dyers, &c.*, iv. 84). With dinitrophenol the following reaction occurs:—$C_6H_3(NO_2)_2OH + Br_2 = HBr +$

$C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows:—
$C_6H_2(NO_2)_3OH + Br_2 = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH$.[1]   In
each case two atoms of bromine enter into the reaction, with for-
mation of a bromo-dinitrophenol (the same in each case) and one
molecule of hydrobromic acid. But in the case of picric acid
nitric acid is formed in addition, and hence the acidity of the
liquid at the end of the reaction would be greater the larger the
proportion of picric acid present. If the bromo-dinitrophenol and
excess of bromine[2] were removed by agitation with ether or
similar solvent, the acidity of the aqueous liquid could be ascer-
tained with great accuracy by titration with standard alkali.

The author found the reaction between bromine and dinitro-
phenol to occur instantaneously, but in the case of picric acid it
was gradual. In twelve hours it was complete, but in the course
of a few minutes almost nothing. This fact enables the reaction
with bromine to be utilized for the direct determination of the
dinitrophenol, instead of for its indirect estimation (by determin-
ing the picric acid), as when the acidity is ascertained. The fol-
lowing method of operating was found by the author to be the
most satisfactory:—1 gramme of the sample of picric acid is dis-
solved in about 100 c.c. of warm water. A saturated solution of
bromine in water is diluted with twice its measure of water in a
large tapped and stoppered separator, and from this run into a
Mohr's burette. From this burette, a definite volume of the
bromine solution, which is approximately of 1 per cent. strength,
is run into a flask and an equal measure into another similar
flask, both of which are immediately closed. The picric acid
solution is then poured into one of the flasks, the last drops rinsed
in without delay, and then an excess of a solution of potassium
iodide at once added to the contents of both flasks. The liberated
iodine is then determined by titration with a decinormal solution
of sodium thiosulphate (hyposulphite) in the usual way.[3] From
the difference in the volume of the solution required in the two
experiments the amount of bromine which has reacted with the
dinitrophenol is easily found. *Dinitrophenol* reacts with 86.96 per

[1] See footnote on page 116, referring to bromo-dinitrophenol as an explosive.

[2] If preferred, before extracting with ether the excess of bromine may be got rid
of by adding potassium iodide and then sufficient sodium thiosulphate to react
with the iodine liberated.

[3] The author found iodine to be wholly without action on solutions of either
mono-, di-, or tri-nitrophenol.

cent. of bromine, taking up 43.48 per cent. *Mononitrophenol*, if present, which is improbable, would react with 230.2 per cent. of bromine, taking up 115.1 per cent. to form the compound $C_6H_2Br_2(NO_2).OH$. The author has verified these reactions by experiments on specially prepared mono- and dinitrophenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

Commercial picric acid often contains particles of a red color These are often attributed to the presence of dinitrophenol, but from an observation of T. W h i t a k e r (*Jour. Soc. Dyers, etc.*, iv. 87) it is not improbable that they consist of a *nitrosophenol*.

A method for the detection of picric acid is given by A. R y n i s k a (*Zeit. Anal. Chem.*, 1897, 813). The substance is macerated for several hours with water, acidified with sulphuric acid, then mixed with three volumes of 95 per cent. alcohol, and digested for 24 hours at 50–60° C. After filtration and evaporation of the alcohol, any fat is removed by shaking with light petroleum, and the liquid is then acidified with hydrochloric acid and shaken repeatedly with ether. Urine, which in cases of poisoning with picric acid is always colored reddish-brown by the presence of picramic acid, may be extracted with ether after simply acidifying. The residue obtained by evaporating the ether is then tested for picric acid by (1) the isopurpuric reaction (blood-red color on warming with potassium cyanide and soda); (2) the picramic acid reaction (blood-red color on heating with soda and grape-sugar), or, better (3) soda and sodium sulphide; (4) ammoniacal copper solution (yellow-green crystals which polarize light); and (5) by dyeing white wool. The limit of sensitiveness of the five reactions is 1 : 5000, 1 : 7000, 1 : 12500, 1 : 80000, and 1 : 110000 respectively. Reactions (2) and (5) are less sensitive in presence of fats and other substances.

METALLIC PICRATES.

As a rule, the picrates are possessed of but little solubility. They are yellow in color, and crystallize well. Many of them explode violently when heated or struck, and hence they are employed in admixture with metallic chlorates or nitrates for the blasting charge of shells. (See footnote on page 116.)

Potassium picrate, $C_6H_2(NO_2)_3.OK$, forms long yellow needles when a strong solution of picric acid is neutralized by carbonate or hydroxide of potassium. The salt requires 288 of cold or 14 parts

of boiling water for solution, and in alcohol is nearly insoluble. The aqueous solution is much more strongly colored than a solution of free picric acid of corresponding strength. When heated, potassium picrate becomes red and explodes like gunpowder, and when strongly struck it detonates violently.

Sodium picrate is readily soluble in pure water, but nearly insoluble in solution of carbonate of sodium or caustic soda.

Ammonium picrate crystallizes in rhombic scales which are somewhat more soluble than the potassium salt. It has been suggested for use as an antipyretic.

Lead picrate crystallizes in brown needles soluble in 119 parts of cold water. In admixture with nitre it is employed as an explosive. A rough mixture of picric acid with red lead or litharge detonates violently when strongly struck.[1]

Nitrosamine Red[2] is a dyestuff which has but lately been introduced. It is made by treating the chloride of para-nitro-diazobenzene with caustic soda. Its constitution has not been exactly determined, but it evidently conforms to one of two formulæ, as is shown by the following diagrams. It may be either:
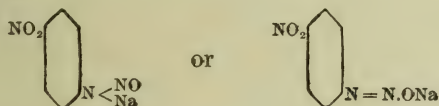
The first is a nitro-nitroso-compound, whereas the second is a true diazo-derivative. Its method of formation tends to the adoption of the second formula as the one most probably correct. Nitrosamine red comes into commerce in the form of a yellow paste, which forms a yellow solution with water. On the addition of acids to the aqueous solution the free paranitrophenyl nitrosamine is precipitated. The latter is gradually converted by an excess of acid into a salt of a diazo-derivative of nitro-benzene. Nitrosamine red dyes wool a clear yellow; and is dyed on cotton with beta-naphthol, giving brilliant red shades (paranitraniline red).

The **Mikado Golden Yellows** or **Direct Yellows** are condensation products of para-nitrotoluol sulphonic acid and

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[1] This appears to be the essential constituent of the new explosive *lyddite*, so extensively used by the British army.

[2] *Ber.* xxvii. p. 514.

caustic soda with hydrochloric, hydrobromic, or nitric acids.[1]
They occur in the form of yellow powders, yielding a yellow solu-
tion in water, and are insoluble in alcohol. The addition of
sodium hydrate to the aqueous solutions produces a yellow preci-
pitate, whereas hydrochloric acid gives a brown color. Strong
sulphuric acid dissolves the dyestuff with an orange color, which
changes to yellow on dilution with water. These dyestuffs yield
very fast colors on cotton, which fibre they dye directly. The
shades produced are very bright yellows which possess good fast-
ness to washing, acids and alkalies, and are fairly fast to light.
These dyestuffs may also be employed for dyeing animal fibres,
being dyed from a neutral or slightly acid bath. The shades pro-
duced are fast to washing but are considerably altered by both
acids and alkalies.

Nitrophenol-sulphonic Acid.

The mono- and dinitro-derivatives of phenol are, like phenol
itself, acted on by strong sulphuric acid with formation of s u l -
p h o n i c   a c i d s. If a mono-nitrophenol be sulphonated, the
product can be converted into a dinitrophenol-sulphonic acid by
careful nitrification, but if the treatment with nitric acid be
pushed to an extreme the product is invariably picric acid, the
sulphonic group being eliminated.

The sulphonated nitrophenols furnish two classes of salts:—
normal salts in which only the hydrogen of the sulpho-group is
replaced by metals, and *basic salts* in which the hydrogen of the
hydroxyl group is also replaced. The former salts are yellow, but
the latter are red, and often of great beauty.

Nitrocresols.

When the mixture of isomeric c r e s o l s, $C_6H_4(CH_3).OH$, from
coal-tar, forming the fraction of the phenolic bodies boiling at
about 200° C., is treated with nitric acid, the orthocresol and
paracresol are converted respectively into d i n i t r o - o r t h o -
c r e s o l and d i n i t r o - p a r a c r e s o l, respectively. The meta-
cresol, which is the most abundant of the isomeric cresols, is, on
the other hand, converted into t r i n i t r o - m e t a c r e s o l, melting
at 160° The isomeric dinitrocresols can be separated by taking
advantage of the difference in the solubility of their barium salts.
They may also be obtained by acting on the corresponding tolui-

[1] *Ber.* xxvi., p. 2234.

dines in ice-cold hydrochloric acid solution with sodium nitrite, when d i a z o t o l u e n e c h l o r i d e, $C_6H_4(CH_3)N:NCl$, is formed, and if this be poured into hot nitric acid the d i n i t r o c r e s o l is formed, and crystallizes out on cooling.

DINITROCRESOLS, $C_6H_2(CH_3)(NO_2)_2.OH$, in their physical and general properties closely resemble picric acid, but are volatile and more readily explosive.[1] The salts of dinitro-orthocresol are generally yellow; but those of the para-compound are usually red, and soluble in water with more or less orange color.

Victoria Yellow is a mixture of the s o d i u m salts of dinitro-ortho- and dinitro-para-cresol, $C_6H_2(CH_3)(NO_2)_2.ONa$.

The dinitrocresylates form soluble reddish-yellow powders which dissolve in strong sulphuric acid with a pale yellow color. They are violently explosive in a dry state. The dinitrocresylates closely resemble the picrates, but on adding hydrochloric acid to the cold aqueous solution the liquid is decolorized; or if sufficiently concentrated, yields a precipitate of free dinitrocresol in pale yellow needles, and the liquid obtained on filtering in the cold is colorless, whereas that yielded by a picrate has a marked yellow color. Similarly, hydrochloric acid decolorizes a tissue dyed with a dinitrocresylate, the yellow color being restored by washing. Warm water removes Victoria yellow from the fibre, and the solution is decolorized by hydrochloric acid as described above.

Solutions of Victoria yellow are unchanged by caustic soda and ammonia, but on boiling with potassium cyanide yield a brown-red liquid similar to that produced with picric acid.

According to H. F l e c k, dinitrocresol and its salts can be distinguished from picric acid by warming the concentrated solution for a few minutes with hydrochloric acid, and then adding a fragment of metallic zinc. After standing in the cold from half an hour to two hours, the liquid will become a beautiful blue if picric acid be present, or a bright blood-red with dinitrocresol. Mere traces of these coloring matters are said to be recognizable by the test. In examining farinaceous foods for dinitrocresol, etc.,

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[1] A. R y n i s k a (*Zeit. Anal. Chem.*, 1897, 813) gives the following tests to distinguish picric acid from dinitrocresol (saffron substitute). When reduced with stannous chloride and hydrochloric acid, potassium dinitrocresol gives a cherry-red color with ammonia; picric acid a brownish-red. Reduced with zinc and hydrochloric acid, the former gives a bright red color which disappears on standing. Picric acid gives at first a blue color and finally a brownish-green, which remains unaltered.

the substance should be exhausted with alcohol, and the test applied to the residue obtained.

The salts of dinitrocresol are very irritating as well as fugitive, and hence are not now used as dyes.[1]

The salts of dinitrocresol have been employed, under the name of "saffron-surrogate," for coloring butter, cheese, macaroni, etc. For this purpose they are very ill-suited, as they have distinct poisonous properties. T. W e y l (*Ber.*, **xx.** 2835; xxi. 212) found that doses of 0.054 gramme for every kilogramme in weight of the animal experimented upon, suspended in milk or water and poured directly into the stomach, in the case of dogs produced vomiting followed by difficulty of breathing, and finally severe cramp in the extremities, the majority of cases terminating fatally. Administered to rabbits, in doses of 0.54 gramme per kilogramme, dinitrocresol caused convulsions, paralysis of the pupil, and great difficulty in breathing, death ensuing from suffocation in twenty to thirty minutes.

Nitronaphthols.

The two modifications of n a p h t h o l, $C_{10}H_7.OH$, yield on nitrification bodies analogous to those obtained by similar means from phenol and cresol. The d i n i t r o - d e r i v a t i v e of a l p h a - n a p h t h o l is the most important.

DINITROALPHANAPHTHOL, $C_{10}H_5(NO_2)_2.OH$, is obtained from a-naphthylamine, a-$C_{10}H_7.NH_2$, by converting it into the diazo-chloride, which on treatment with nitric acid yields the corresponding dinitronaphthol. It may also be obtained by dissolving a-naphthol in concentrated sulphuric acid, diluting the resulting sulphonic acid with water, adding nitric acid, and heating gently, when the dinitro-derivative is deposited in minute yellow needles. The product may be purified by converting it into its calcium or ammonium salt, which after recrystallization is decomposed by an acid.

Dinitronaphthol forms yellow needles, melting at 138° C., and somewhat readily volatile. It is nearly insoluble in water, but soluble in alcohol and ether. It closely resembles picric acid, and forms a series of beautiful and well-crystallized *salts* yielding golden yellow solutions, which are decolorized by hydrochloric acid, a

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[1] Victoria yellow is also to be met with under the names of *English yellow*, *Victoria orange*, and *aniline orange*. These are acid dyestuffs, but are no longer used to any extent as they are very fugitive and not at all fast to washing.

yellowish-white precipitate of the free acid being produced, soluble in ether. Ammonia is without action. Caustic potash and soda produce orange-red precipitates in strong solutions. Potassium cyanide and ammonium sulphide react as with picric acid.

The *sodium salt* of dinitronaphthol forms readily soluble glittering needles containing $C_{10}H_5(NO_2)_2.ONa + H_2O$, and deflagrates when heated. The *ammonium salt* burns off quietly when heated, and is soluble in alcohol. The *calcium salt* forms yellowish-red crystals of the formula $[C_{10}H_5(NO_2)_2O]_2Ca + 6H_2O$.

The potassium, sodium, ammonium, and calcium salts of dinitronaphthol have been extensively employed as coloring matters under the name of

Naphthol Yellow; NAPHTHALENE YELLOW; MANCHESTER YELLOW; Martius' Yellow; Gold Yellow. This dyestuff occurs as an orange powder or crystal, but sparingly soluble in water, though readily soluble in alcohol. On the addition of hydrochloric acid to the aqueous solution dinitro-alpha-naphthol is liberated as a light yellow precipitate. Sulphuric acid gives a yellow solution in which a light yellow precipitate is found on dilution with water. In an acid bath this body dyes silk and wool (but not cotton) a brilliant yellow color, free from the greenish reflection peculiar to fabrics dyed with picric acid. Owing to the volatility of dinitronaphthol (which is liberated by the acid of the bath), the color marks and rubs off, and hence the employment of naphthalene yellow as a dye has much diminished.

Naphthol yellow is very commonly adulterated with *dextrin* and *sodium sulphate*, the proportion of the latter admixture sometimes reaching 50 per cent. It is sometimes adulterated with *picric acid*, to detect which a sample should be dissolved in water, the cold solution acidulated freely with hydrochloric acid, and the liquid filtered. If picric acid be present the filtrate will have a marked yellow color, and the acid can be obtained in crystals by evaporation.

Naphthol yellow may be distinguished from picric acid by boiling wool in the acidified solution, washing it, heating it with ammonio-sulphate of copper, and again washing. When a fibre or fabric dyed with picric acid is boiled with the alkaline copper solution it turns bluish-green, but if naphthol yellow has been used an olive-green tint results.

When a material dyed with naphthol yellow is wrapped in white paper and heated to 120° C. in an air-bath, part of the yellow color

is transferred to the paper. Hot water or hot dilute ammonia dissolves out the coloring matter, and the yellow solution is decolorized by hydrochloric acid, a yellow-white precipitate being produced (distinction from picric acid).

Naphthol yellow is sometimes employed for coloring butter, cheese, macaroni, mustard, saffron, etc., for which applications its marked poisonous characters render it very unfit.[1] The detection of butter-colorants will be described under "Annatto."

Martius' yellow when used in foods taken into the stomach may be detected in the urine by the following methods:

1. The urine slightly acidified with hydrochloric acid is shaken up with ether. A portion of the ethereal layer is shaken with caustic potash solution. The alkaline liquid is acidified with hydrochloric acid and warmed with some strands of white wool free from fat and mordanted with alum. The wool is colored yellow in the presence of as little as one-millionth gramme of the dyestuff.

2. A portion of the ethereal solution is evaporated to dryness, a drop of potassium cyanide solution is added to the residue, when a red coloration is obtained.

3. Another portion of the residue by evaporation of the ethereal solution is mixed with potassium bisulphate, heated to redness in a glass tube, and the residue dissolved in water. A paper moistened with Guess's reagent and placed in the solution is colored violet.

4. A solution of Martius' yellow, or urine containing it, gives with cobalt chloride and a little caustic soda, a fine green pigment.

5. With stannous chloride and a trace of ammonia, Martius' yellow gives a white precipitate, which becomes rose-red by subsequent treatment with ammonia.

For the recognition of Martius' yellow in the stomach, intestines, etc., these are finely cut up, acidified slightly with hydrochloric acid, and digested for some hours at 40°–50° with absolute alco-

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[1] Comparatively small doses of naphthol yellow are said to cause asthmatic breathing, a considerable rise of temperature (without convulsions), and ultimately death (*Comp. rend.*, 1885, p. 101). According to Weyl (*Ber.*, xxi. 2191), Martius' yellow is well tolerated by rabbits, but small doses proved fatal to dogs. A dog weighing 6850 grms., to which a dose of 0.5 grm. of dinitronaphthol was given on two successive days, and 1 grm. of the sodium salt on the third day, died on the fourth day. Less than 1 grm. given subcutaneously caused the death of a similar dog. On the other hand, naphthol yellow S proved innocuous to dogs in four times these amounts.

hol.   The liquid is filtered, evaporated at a low temperature, made alkaline with caustic potash, filtered, acidified with hydrochloric acid, and shaken out with ether, which solution is then examined as above.

In small doses Martius' yellow does not seem to have any poisonous effect on the human system, and the small quantity that may be found in foods is quite harmless.

Heliochrysin, or SUN GOLD, is the commercial name of an unstable coloring matter consisting of the s o d i u m   s a l t   of t e t r a- n i t r o n a p h t h o l, $C_{10}H_3(NO_2)_4.ONa$.

Nitronaphthol-sulphonic Acids.

When alphanaphthol is warmed with excess of fuming sulphuric acid it yields a t r i s u l p h o n i c   a c i d, which on subsequent treatment with strong nitric acid yields, on cooling, crystals of

DINITRO-ALPHANAPHTHOL-SULPHONIC ACID, $C_{10}H_4(SO_3H)(NO_2)_2OH$. The product is purified by recrystallization.   It forms long yellow needles, readily soluble in warm water, but insoluble in ether. These characters distinguish it from picric acid, dinitro-naphthol, etc.   Its salts are easily crystallizable, said to be non-poisonous, and dye wool and silk (but not cotton) a bright yellow color, which is fast in the light, non-volatile, and does not mark or rub off.   For these reasons the salts have largely replaced picric acid and the dinitro-naphtholates.

Potassium Dinitro-a-naphthol-sulphonate, $C_{10}H_4(SO_3K)(NO_2)_2.OK$, forms an orange-yellow precipitate on mixing a strong solution of the free acid with one of potassium sulphate.   It is sparingly soluble in cold, but readily in hot water.   By boiling it with strong hydrochloric acid the free acid, or, according to some, an *acid salt*, $C_{10}H_4(SO_3K)(NO_2)_2OH$, is formed.

The sodium and ammonium salts of dinitronaphthol-sulphonic acid are freely soluble, but the *barium* and *lead* salts only sparingly so.

The *salts* of dinitronaphthol-sulphonic acid are yellow or orange. On heating, they swell up and emit sparks, but do not deflagrate. The solutions are yellow or brownish-yellow, becoming pale yellow on adding hydrochloric acid, but no precipitate is produced, and the diluted acid liquid is not decolorized by agitation with ether. (Distinction from picric acid, etc.)   With caustic soda an orange-yellow precipitate is formed, soluble on warming.   In strong sulphuric acid the dinitronaphthol-sulphonates dissolve with pale yellow color.   In other reactions they resemble Manchester yellow, but do not volatilize or color their paper envelope at 120° C.

Naphthol Yellow S; NAPHTHOL YELLOW; CITRONIN;[1] ACID YELLOW S; BRILLIANT YELLOW, etc., are names given to the potassium, sodium, ammonium, and calcium salts of dinitronaphtholsulphonic acid. The free acid is also met with under the name of "naphthol yellow" (Levinstein).

Commercial naphthol yellow S varies much in character. Some qualities are practically pure, while others contain sodium sulphate and chloride in notable quantity. C. R a w s o n (*Jour. Soc. Dyers, &c.*, iv. 82) has proposed a method of assay depending on the precipitation of the coloring matter by a solution of night-blue, which is made by dissolving 10 grammes in 50 c.c. of glacial acetic acid, and diluting the liquid to 1 litre. The naphthol yellow is used as a solution containing 1 gramme per litre. The latter solution is added to 10 c.c. of the former until on filtration of a portion of the liquid it is found to have a faint yellow color. The method is similar to that described for the determination of picric acid described on page 117. Two molecules of night-blue react with one of naphthol yellow.

Naphthol yellow S may be adulterated with the cheaper naphthol yellow, and the latter may be detected by adding hydrochloric acid to the aqueous solution: naphthol yellow is precipitated or the solution becomes milky, whereas a solution of pure naphthol yellow S remains clear. If the dry color is treated with ether, naphthol yellow S will not color the liquid even on addition of soda, while naphthol yellow colors the ether yellow and remains yellow on addition of soda.

Nitro-diphenylamines.

On treating diphenylamine with nitric acid it readily yields nitro-substitution products. The t e t r a n i t r o - d e r i v a t i v e, $[C_6H_3(NO_2)_2]_2NH$, mixed with a little of the d i n i t r o - p r o d u c t, forms the coloring matter known as " Citronin." On warming diphenylamine or methyl-diphenylamine with nitric acid, it yields h e x a n i t r o-d i p h e n y l a m i n e, a body of strongly acid character, melting at 238°, the *ammonium salt* of which constitutes the "aurantia" of commerce.

Aurantia, or IMPERIAL YELLOW $[C_6H_2(NO_2)_3]_2.N(NH_4)$, forms

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[1] The name citronin is used both for naphthol yellow S and the product obtained by acting with nitric acid on diphenylamine, as also for the azo-dye called a z o-f l a v i n e.

a reddish-yellow crystalline powder, or brownish-red crystals which decrepitate on heating and sometimes deflagrate slightly. Aurantia is easily soluble in water to form a solution which is red when concentrated, but yellow when diluted. On addition of hydrochloric acid, the aqueous solution yields a sulphur-yellow flocculent precipitate of free hexanitro-diphenylamine, and on filtering a nearly colorless liquid is obtained. The precipitate dissolves on agitation with ether. An acid solution of stannous chloride also precipitates the free acid, but the yellow precipitate becomes dark brown on boiling. Copper salts also turn the solution of aurantia brown. Solutions of aurantia are darkened or reddened by caustic alkalies, and if concentrated a dark red precipitate is produced. Solid aurantia is not changed in color by strong sulphuric acid.

Aurantia does not appear to be entirely harmless in its physiological action, as even dilute solutions of the dyestuff produce painful blisters on the skin. However, there seems to be an isomeric hexanitro-diphenylamine which is harmless.

On the fibre, hydrochloric acid turns the color due to aurantia a lighter yellow. Ammonia and caustic soda produce but little change. The dark brown coloration produced on warming with stannous chloride is the most characteristic reaction of aurantia.

Aurantia has been almost completely replaced by the azo-colors, and is only used in leather dyeing.

(b) Nitroso- and Isonitroso-coloring Matters.

By treating an aqueous solution of phenol with potassium nitrite and acetic acid, a body is formed which was formerly supposed to be n i t r o s o - p h e n o l, $C_6H_4(NO).OH$, but which more recent research has shown may more correctly be regarded as q u i n o n-

o x i m e, $C_6H_4O(NOH)$, or $C_6H_4 \begin{cases} O \\ | \\ N.OH. \end{cases}$

The orthoquinonoximes dye on metallic mordants, while the other quinonoximes do not. These colors are permanently decolorized by the action of reducing agents, amidophenols being formed. The nitroso-compounds are dyed almost exclusively on iron mordants, invariably giving green shades with this metal which are notable for their great fastness to light. Handsome brown shades are obtained by the use of cobalt mordants.
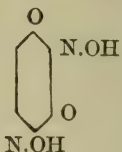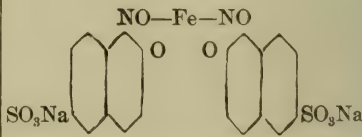
QUINONOXIME is best prepared by treating phenol dissolved in thirty parts of water with rather more than the theoretical quantity
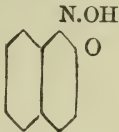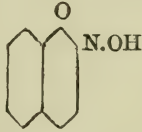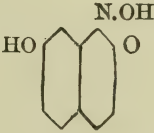
of nitrosulphonic acid, prepared by passing nitrous fumes into concentrated sulphuric acid. The crystals which separate are filtered off without delay. Quinonoxime forms a green solution in hot water, separating in nearly colorless needles by rapid cooling, or in thin, brownish-green plates if the liquid be cooled slowly. It dissolves in alkalies with a brown color, and on acidulating the solution separates as a nearly white amorphous precipitate, soluble in alcohol or ether with a green color.

Quinonoxime, if moist, rapidly turns brown on exposure to air. When heated to 120°–130° C. it decomposes with slight detonation. By ferricyanides in alkaline solution it is oxidized to p a r a n i t r o p h e n o l. When quinonoxime is dissolved in phenol, strong sulphuric acid added, and the liquid warmed to about 40° C., a dark cherry-red or brown solution is obtained, which on addition of water yields a flocculent brown precipitate, known as "Liebermann's phenol dye-stuff." This body dissolves in alkalies and sulphuric acid with a fine blue color, and has the formula, $C_6H_4(OH).N:(O.C_6H_5)_2$.

Orcin in the same manner yields coloring matters which are closely related to the orchil colors, especially orceïn. But the only coloring matter of any technical importance is the one derived from resorcin.

The following table shows the nitroso- and iso-nitroso- colors:

COMMERCIAL NAME.	CHEMICAL NAME.	CONSTITUTIONAL FORMULA.
Dinitrosoresorcinol. Resorcin Green. Dark Green. Solid Green. Chlorin. Russian Green. Alsace Green. Fast Myrtle Green.	Dinitrosoresorcinol. Dioximidoquinone.	
Naphthol Green B.	Ferrous-sodium salt of nitroso-beta-naphthol-beta-monosulphonic acid.	

COMMERCIAL NAME.	CHEMICAL NAME.	CONSTITUTIONAL FORMULA.
Nitrosonaphthol. Gambin Y. Alsace Green J.	Alpha-nitroso-beta-naphthol.	
Gambin R.	Beta-nitroso-alpha-naphthol.	
Dioxin. Gambin B.	Mononitroso-di-oxynaphthalene.	

DINITROSORESORCINOL. $C_6H_2O_2(NOH)_2$ or
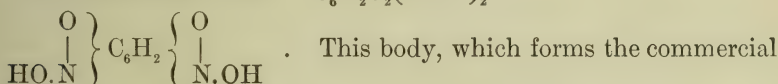
$$\left. \begin{array}{c} O \\ | \\ HO.N \end{array} \right\} C_6H_2 \left\{ \begin{array}{c} O \\ | \\ N.OH \end{array} \right.$$. This body, which forms the commercial

coloring matter known as *resorcin green* or *solid green*, is obtained in a manner similar to quinonoxime, substituting resorcinol for phenol. It forms yellowish-brown or green plates, or a greyish-brown powder. The commercial product is sold as a dark grey paste, as the dry powder is said to be explosive. It dissolves with difficulty in cold water, but readily in hot. It deflagrates slightly when heated to 115°. Dinitrosoresorcinol has acid characters. It decomposes carbonates, and to some extent acetates, and forms a series of alkali-metal salts, of which the n o r m a l are soluble, and the a c i d, of the type $C_6H_2O_2(NOH)(NONa)$, are sparingly soluble, green, crystalline powders.

By the action of resorcinol and sulphuric acid on dinitrosoresorcinol, a z o r e s o r u f i n is formed, a body which is analogous to the Liebermann's dye-stuff (see above) obtained in a similar manner from phenol.[1]

[1] In practice, 1 part of resorcinol is dissolved in 5 parts of strong sulphuric acid, and the solution gradually treated with 8 parts of nitrosulphonic acid made by

Naphthol Green B is the s o d i u m-f e r r o u s s a l t of n i t r o-
s o b e t a n a p h t h o l - s u l p h o n i c a c i d (Schäffer's acid).   It
is prepared by the action of nitrous acid on betanaphtholsulphonic
acid S, and combining the product formed with soda and ferrous
oxide.   It forms a dark green powder, which leaves, on ignition,
a residue containing iron and sulphides.   The coloring matter
dissolves in water with yellowish-green coloration, the solution
being unchanged by hydrochloric acid, but rendered bluish-green
by alkalies.   In concentrated sulphuric acid, naphthol green dis-
solves with a yellowish-brown color, the solution becoming yellow
on dilution, and then giving a blue coloration or precipitate both
with ferro- and ferri-cyanides.

Gambin Y or NITROSONAPHTHOL is formed by the action of
nitrous acid on betanaphthol.   It is an olive-green paste, slightly
soluble in water with a yellow color, the solution remaining unal-
tered by hydrochloric acid, but caustic soda produces a greenish-
yellow fluorescence.   It is soluble in alcohol, giving an orange
solution.   In concentrated sulphuric acid it dissolves to a dark
brown solution which gives a flocculent precipitate on dilution
with water.

Gambin R is isomeric with the above, being obtained in the
same manner from alphanaphthol.

Dioxin is produced by the action of nitrous acid on (2:7)
dioxynaphthalene.   It is a reddish-brown paste, very sparingly
soluble in water, but dissolving in caustic soda with an intense
brown color; also soluble in alcohol, giving an orange solution.
With concentrated sulphuric acid a green solution is obtained,
which yields a red precipitate on dilution with water.

2. Azoxy-Coloring Matters.

If nitro-benzene is treated with moderate reducing agents in
alkaline solution, there are formed intermediate reduction products
before the azo-compounds are reached.   These intermediate deri-
vatives are termed a z o x y-compounds, and possess the structure
$-\!\!\!\!\begin{array}{c}N\\N\end{array}\!\!\!\!>O$.
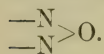
gradually dissolving sodium nitrite in twenty times its weight of strong sulphuric
acid.   The fine blue solution is heated to 140° till violet, when it is cooled and
diluted with water.   The precipitate may be purified, if desired, by treating it
with sodium carbonate, evaporating the solution to dryness, and treating the resi-
due with alcohol, which dissolves the sodium compound of the coloring matter.

If nitrobenzene, for example, is reduced with zinc dust and ammonia a z o x y - b e n z e n e is formed, having the formula,

$$\left.\begin{array}{c} C_6H_5N \\ | \\ C_6H_5N \end{array}\right\rangle O.$$

Should the reduction be carried further, or stronger reducing agents be employed, a z o- and h y d r a z o-derivatives will be found. The azoxy-coloring matters do not form a very extensive group of dyestuffs, nor a very important one, and are often considered as a class under the azo-colors. The azoxy-derivatives are readily converted into the azo-bodies by reducing agents, and in turn can be produced by the oxidation of amido-compounds.

Azoxybenzene. $(C_6H_5)_2N_2O.$

This body is produced by the action of mild reducing agents on nitro-benzene, or by the oxidation of aniline. It crystallizes in long, yellow needles, soluble in alcohol and ether, but not in water. Its melting point is 36°, but it cannot be distilled as it decomposes into azo-benzene and aniline. By heating with sulphuric acid a molecular re-arrangement occurs with the formation of oxyazobenzene.

Sun Yellow. CURCUMIN S.

This dyestuff is also sold under the names of J a u n e s o l e i l and m a i z e, and has the formula:
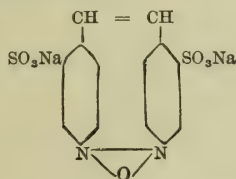
It is, therefore, the sodium salt of azoxy-stilbenedisulphonic acid.[1]

Curcumin S is produced by the action of sodium hydrate on paranitrotoluenesulphonic acid. It is a brown powder soluble in water giving a brownish-yellow solution. With sulphuric acid it gives a violet solution which changes to yellow on dilution with water. Hydrochloric acid gives a brown precipitate from the aqueous solution; sodium hydrate an orange precipitate.

Direct Yellow G is the sodium salt of dinitrosostilbenedisulphonic acid. It may be represented by the formula:

[1] The corresponding ammonium salt is called c u r c u m i n W.

$$CH(1)C_6H_3 \begin{cases} (2)SO_3Na \\ (4)NO \end{cases}$$
$$\|$$
$$\|$$
$$CH(1)C_6H_3 \begin{cases} (4)NO \\ (2)SO_3Na \end{cases}$$
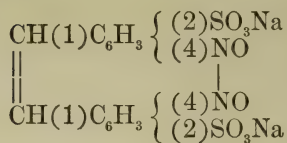
It is a brown powder, soluble in water with an orange color. The addition of caustic soda to the aqueous solution produces a yellow precipitate, as does also hydrochloric acid. It dissolves in strong sulphuric acid with a red color, which changes to yellow on dilution with water.

Mikado Oranges G, R, 2 R, 3 R, 4 R, and **5 R,** and **Mikado Yellow** are prepared by boiling paranitrotoluene-sulphonic acid with alkalies in the presence of certain oxidizable substances such as glycerin, pyrogallic acid, etc. Their composition has not yet been ascertained. They occur as orange powders, soluble in water with an orange color. On the addition of hydrochloric acid to the aqueous solution a brown precipitate is produced; caustic soda gives a yellow precipitate. Strong sulphuric acid dissolves the dyestuff to a blue solution, which gives a brown precipitate on dilution with water.

Mikado Brown, B, 3 GO and **M,** are dyestuffs produced in a manner similar to the above. They are brown powders, giving a brown solution in water. Caustic soda with the aqueous solution produces but a very slight precipitate; hydrochloric acid gives a brown precipitate. Strong sulphuric acid dissolves the dyestuff to a dark red solution, which gives a brown precipitate on dilution with water.

3. Hydrazo Derivatives.

Hydrazo-compounds may be considered as derivatives of hydrazine,[1] NH_2—NH_2, and they possess the group —$NH.NH$—. They may also be considered as reduction products of the azoxy- and azo-compounds.

Hydrazobenzene,[2] $C_6H_5NH.NH.C_6H_5$, is obtained by the action of reducing agents on azobenzene. It is readily soluble in alcohol and ether, and possesses an odor resembling camphor. It crystallizes in colorless plates, melting at 131°. On distillation it is decomposed into azo-benzene and aniline. Oxidation readily converts hydrazobenzene into azobenzene. Hydrazobenzene gives

[1] See Vol. III, pt. II, p. 27.

[2] See Vol. III, pt. II, p. 89.

the characteristic phenylhydrazine reaction[1] with aldehydes, forming compounds known as hydrazoïnes. It combines with acetic acid esters, giving rise to pyrazol derivatives.[2] When treated with concentrated sulphuric acid, a molecular re-arrangement occurs and the isomer b e n z i d i n is produced,[3] which has the formula $NH_2.C_6H_4.C_6H_4.NH_2$. Nitro- and amido-hydrazobenzenes are known, and also the sulphonic acid. Hydrazotoluenes, $CH_3.C_6H_4.NH—NH.C_6H_4.CH_3$, have also been prepared. All of these hydrazo-compounds are converted into diphenyl derivatives in a matter similar to the conversion of hydrazobenzene into benzidine.

Tartrazin is the sodium disulphonate of diphenyl-osazone-dioxytartaric acid, and may be represented by the following formula:

$$
\begin{array}{l}
COOH \\
| \\
C = N.NH.C_6H_4.SO_3Na \\
| \\
C = N.NH.C_6H_4.SO_3Na \\
| \\
COOH.
\end{array}
$$
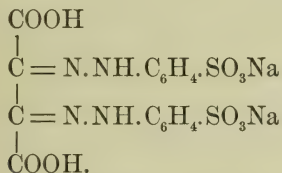
It is prepared by the action in alkaline solution of phenyl-hydrazine-parasulphonic acid on dioxytaric acid. According to Nietzki tartrazin has the following constitution:
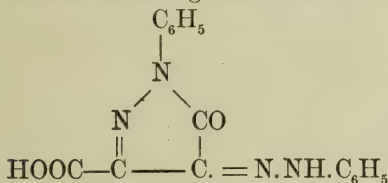
being a derivative of pyrazolon, though this hardly agrees with the fact that reducing agents resolve it into sulphanilic and diamido-succinic acids. It forms a beautiful orange-yellow powder, soluble in hot water to a golden-yellow solution, which if concentrated deposits a yellow precipitate on cooling. On adding alcohol to the concentrated aqueous solution a crystalline precipitate is obtained. The solution is not changed by dilute acids, but becomes reddish on adding caustic soda. Stannous chloride produces a yellow precipitate, soluble in oxalic acid. Barium chloride gives

[1] See Vol. III, pt. II, p. 30.
[2] See Vol. III, pt. II, p. 31.
[3] See Vol. III, pt. II, p. 89.

a yellow precipitate, but calcium chloride occasions no change. Concentrated sulphuric acid dissolves the solid dye with a yellow color, which is unchanged on dilution. Tartrazin precipitates the coal-tar bases very completely,[1] and dyes wool yellow in an acid bath.

Other dyestuffs of the tartrazin class have been prepared by substituting for phenyl-hydrazine sulphonic acid its homologues and the naphthylhydrazine sulphonic acids, and using instead of dioxytartaric acid such double ketones as benzil and phenanthraquinone (*Jour. Soc. Dyers, etc.*, iii. 132; iv. 109). Thus *isatin-yellow* is obtained by the action of isatin on phenylhydrazine-parasulphonic acid, and *phenanthrene-red* by the reaction of one molecule of phenanthraquinone on two of naphthyl-hydrazine-sulphonic acid. The constitution of all these dyestuffs is analogous, the phenanthraquinone compound having its two benzene rings directly united in addition to being connected through the —C—C— group, which results in the reddish-yellow color of the dyestuff. The tartrazins closely resemble the mixed azo-dyes, as may be seen by comparing the constitution of the two classes:

$$
\begin{array}{ll}
\text{COOH} & \text{COOH} \\
\;\mid & \;\mid \\
\text{C}=\text{N.NH.C}_6\text{H}_5 & \text{CH}-\text{N:N.C}_6\text{H}_5 \\
\;\mid & \;\mid \\
\text{C}=\text{N.NH.C}_6\text{H}_5 & \text{CH}-\text{N:N.C}_6\text{H}_5 \\
\;\mid & \;\mid \\
\text{COOH} & \text{COOH}
\end{array}
$$
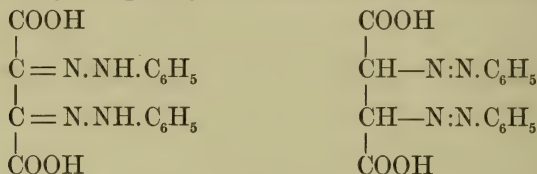
the first being the formula of the osazone of unsulphonated tartrazin, and the second that of a mixed azo-dye.

Azarin S is a compound of dichlorphenolazobetanaphthol with ammonium bisulphite. It is a yellow paste, smelling of sulphurous acid; it is sparingly soluble in water with a yellow color, with which solution caustic soda gives a violet precipitate, and hydrochloric acid an orange precipitate. The dye dissolves in strong sulphuric acid with a magenta red color, the solution giving a brown precipitate on dilution with water. It is chiefly employed in calico-printing, and its shades are very fast to soap and fairly so to light.

4. Azo- and Tetrazo-Coloring Matters.

Of late years a series of very brilliant and fast dyes have come into use, which are generally known as a z o - d y e s.

[1] W. R. Richardson, *Jour. Soc. Dyers, etc.*, iii. 2.

All these substances contain the divalent group —N : N—. If both of the free bonds be satisfied by the radical p h e n y l the substance known as a z o - b e n z e n e, $C_6H_5.N:N.C_6H_5$, results; or if the two radicals be not identical a "mixed" azo-compound results, such as may be typified by b e n z e n e - a z o - t o l u e n e, $C_6H_5.N:N.C_7H_7$.

The azo-compounds in general are obtained by the reduction of nitro-compounds in alkaline solution. Reducing agents, such as sodium amalgam in alcoholic solution, zinc dust with sodium hydrate, or stannous chloride with sodium hydrate are most frequently employed. All nitrobenzene compounds react in this manner, with the exception of nitro-naphthalene.

The azo-compounds are usually yellow or brown solids. They are readily converted into benzidine by the action of stannous chloride in acid solution, but otherwise they are quite stable, and may be chlorinated, nitrated, and sulphonated.

Amido-azo-compounds are produced by the reduction of the corresponding nitro-azo-derivative. Oxy-azo-compounds are corresponding phenols, having the structure $C_6H_5.N:N.C_6H_4.OH$. These amido and phenol groups seem to determine the dyeing property of the azo-compounds, the latter in themselves not being dyestuffs. The azo-dyes are therefore either amido-compounds, the so-called azo-bases which form salts with acids; or phenol-compounds, the azo-acids, which form salts with bases. The dyestuffs are usually brought into commerce as the sulphonic acids of the corresponding azo-bases and azo-acids. The azo-compounds in general are acid dyeing colors, and are produced by combining diazotized aromatic amines and their sulphonic acids with aromatic amines or phenols and their sulphonic acids.

The azo-compounds for the most part give rise to yellow, orange, red, brown, violet, and black shades. The azo-group does not appear to be able to yield green coloring matters.

Azobenzene. $C_6H_5.N_2.C_6H_5$.

This body is prepared by the reduction of nitrobenzene with nascent hydrogen. Acetic acid and iron may be employed as the reducing agent, or preferably an alkaline reagent, such as zinc and alcoholic potash, sodium stannite, or sodium amalgam. If sodium amalgam be employed, the intermediate product a z o x y - b e n z e n e is first obtained, while too-long continued treatment causes the formation of h y d r a z o b e n z e n e and the isomeric body

b e n z i d i n e, and the former of these may in turn be converted
into a n i l i n e. These bodies form a continuous series, thus:—

Nitro-benzene,	$C_6H_5NO_2 \times 2 = C_{12}H_{10}N_2O_4$	
Azoxy-benzene,	$C_{12}H_{10}N_2O$	
Azo-benzene,	$C_{12}H_{10}N_2$	
Hydrazo-benzene,	$C_{12}H_{12}N_2$	
Amido-benzene (aniline),	$C_6H_7N \times 2 = C_{12}H_{14}N_2$.	
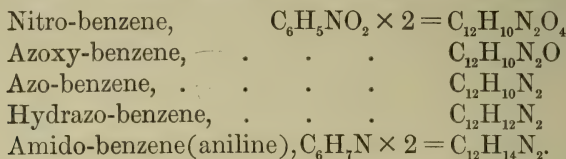
By treating aniline with potassium permanganate, the reverse
series of reactions may be obtained, at least so far as oxidation to
azoxy-benzene; and among the secondary products is found *aniline
black*, which has the same percentage composition as azo-benzene.

Azobenzene crystallizes in large yellowish-red laminæ, sparingly
soluble in water, but readily in alcohol and ether. The alcoholic
solution has an intense yellow color, but no dyeing powers. Azo-
benzene melts at 65.5°, and distils at 293°. Treated in alcoholic
solution with sulphuretted hydrogen, it is converted into hydrazo-
benzene. With bromine, azobenzene forms the additive com-
pound $C_{12}H_{10}Br_2N_2$, and with nitric acid reacts to form mono- and
di-nitro-derivatives. *Nitro-azobenzene* $C_6H_5.N_2.C_6H_4(NO_2)$, can be
reduced to amido-azobenzene, $C_6H_5.N_2.C_6H_4(NH_2)$, and this on
treatment with nitrous acid and warm water yields o x y a z o -
b e n z e n e, $C_6H_5.N_2.C_6H_4(OH)$,[1] which is made by digesting diazo-
benzene nitrate with barium carbonate, or by the action of
concentrated sulphuric acid on azoxybenzene. It crystallizes in
orange-yellow needles melting at 148° C. These bodies dye silk
or wool orange or yellow, but offer little resistance to the action of
acids.

Diazobenzene Compounds. $C_6H_5.N:N.X.$

When the free bond of the second nitrogen atom of the group
—N: N— is satisfied by a simple atom or an acid or basic group,
instead of by a hydrocarbon radical, the substance is said to be a
"d i a z o - c o m p o u n d." Thus the body represented by the
formula $C_6H_5.N:N.Cl$ is called d i a z o - b e n z e n e c h l o r i d e,[2]
and is the type of a large number of interesting bodies.

[1] This body is preferably called h y d r o x y - a z o b e n z e n e. It must not be
confounded with a z o x y - b e n z e n e, $\left.\begin{array}{c} C_6H_5.N \\ C_6H_5.N \end{array}\right\}$ O. It evidently has the hy-
droxyl group in the para position with reference to the azo-group; for oxyazo-
compounds containing the hydroxyl group in the ortho-position are most probably
quino-hydrazones.

[2] Hence azobenzene, $C_6H_5.N:N.C_6H_5$, is diazobenzene phenylide.

Free d i a z o b e n z e n e is not known, nor does the h y d r i d e, $C_6H_5.N_2.H$, appear to be obtainable. The h y d r o x i d e, $C_6H_5.N_2.OH$, is a highly unstable, explosive, yellow oil, which reacts with acids to form a highly interesting series of salts. They are mostly colorless, crystalline bodies, which turn brown rapidly on exposure to air. They are readily soluble in water, sparingly in alcohol, and are precipitated from their alcoholic solutions by ether. Most of them are unstable, and decompose with explosion when heated or struck. The chlorochromate explodes more violently than nitroglycerin. By many reagents they are decomposed in a peculiar manner, usually with evolution of free nitrogen, as in the following examples:—

1. $\underset{\text{Diazo-bromide}}{C_6H_5.N_2.Br} + H_2O = \underset{\text{Phenol}}{C_6H_5.OH} + N_2 + HBr.$

2. $\underset{\text{Diazo-nitrate}}{C_6H_5.N_2.NO_3} + \underset{\text{Alcohol}}{C_2H_5OH} = \underset{\text{Benzene}}{C_6H_5H} + N_2 + HNO_3 + \underset{\text{Aldehyde}}{C_2H_4O.}$

3. $\underset{\text{Diazo-acid sulphate}}{C_6H_5.N_2.HSO_4} + HI = \underset{\text{Phenyl iodide}}{C_6H_5I} + N_2 + H_2SO_4.$

4. $\underset{\text{Diazo-chloride}}{C_6H_5.N_2.Cl} + Cu_2Cl_2 = \underset{\text{Phenyl chloride}}{C_6H_5Cl} + N_2 + CuCl_2.[1]$

5. $\underset{\text{Diazo-perbromide}}{C_6H_5.NBr:NBr_2} + C_2H_5.OH = \underset{\text{Phenyl bromide}}{C_6H_5Br} + N_2 + C_2H_4O + 2HBr.$

Diazobenzene Chloride, $C_6H_5.N_2.Cl$, is obtained in solution by gradually adding sodium nitrite to an ice-cold, dilute solution of one molecule of aniline and two of hydrochloric acid, the liquid being well stirred during the addition. The conclusion of the reaction is known by the evolution of nitrous acid, recognizable by its turning blue a piece of paper moistened with a solution of potassium iodide and starch and held over the liquid. Diazobenzene chloride is only known in solution, which undergoes decomposition when heated, but it forms crystalline compounds with platinic and stannic chlorides.

Diazobenzene Nitrate, $C_6H_5.N_2.NO_3$, is prepared by passing a slow stream of nitrogen trioxide gas (prepared from starch or arsenious oxide and nitric acid) into a paste of aniline nitrate and water, cooled by immersion in a mixture of ice and salt, until the addition of caustic alkali to a sample quantity no longer liberates aniline in oily globules. The liquid is filtered, and the diazobenzene

---

[1] By substituting cuprous bromide, iodide, or cyanide for the chloride, the corresponding haloid compounds of phenyl may be obtained. The cyanide reacts with caustic potash to form potassium b e n z o a t e, C_6H_5COOK, and a m m o n i a.

nitrate precipitates from the filtrate by adding three volumes of alcohol and some ether. Diazobenzene nitrate separates in yellow needles which are readily soluble in water, and slightly so in alcohol, but insoluble in ether. In the dry state, when gently heated or struck, it explodes more violently than fulminating mercury, and hence should be preserved under ether.

Acid Diazobenzene Sulphate, $C_6H_5.N_2.HSO_4$, is obtained by adding diluted sulphuric acid (1:2) to a concentrated aqueous solution of the last salt. Alcohol (3 volumes) and ether are then added, and the heavy liquid which separates redissolved in strong alcohol and precipitated by adding ether, the process being repeated till the sulphate separates in a crystalline form. The salt forms white, deliquescent prisms, which decompose in the air and detonate at about 100°.

Diazobenzene-sulphonic Acid, $C_6H_4\left\{\begin{array}{l}.N:\\.SO_3\end{array}\right\}:N.$ This body, of which three modifications exist, is not well named, as it is really the anhydride of the true s u l p h o n i c a c i d, $C_6H_4(SO_3H).N_2.OH$. The para-compound, which is the only one of practical importance, is obtained by adding rather more than the calculated quantity of sodium nitrite to a solution of sulphanilic acid (para-amidobenzene-sulphonic acid), $C_6H_4(SO_3H).NH_2$, in dilute caustic soda, and pouring the mixture into cooled, dilute sulphuric acid. The diazo-sulphonic acid separates in white crystals, insoluble in cold water, but readily soluble at 60°–70°. It is decomposed by water at a higher temperature, with formation of para-phenolsulphonic acid, while boiling alcohol converts it into benzene-sulphonic acid, $C_6H_5.SO_3H$.

DIAZO-AMIDOBENZENE, $C_6H_5N:N.NH.C_6H_5$. This body is formed when nitrous gas is passed into a solution of aniline in alcohol, and may be regarded as resulting from the action of aniline (amidobenzene) on diazobenzene hydroxide:—$C_6H_5.N_2.OH + NH.$ $H.C_6H_5 = C_6H_5.N_2.NH.C_6H_5 + H_2O.$ Diazo-amidobenzene is also formed when a cold concentrated solution of diazobenzene nitrate is dropped gradually into strong ammonia or mixed with aniline; or by adding a solution of diazobenzene chloride to aniline kept cool, and treating the product with sodium acetate, when the diazo-amidobenzene is thrown down as a yellow precipitate. It may be obtained more directly by adding gradually a cooled solution of sodium nitrite to a mixture of one molecule of aniline and one of aniline hydrochloride, when it is precipitated. Diazo-amidoben-

zene crystallizes in golden yellow scales, melts at 91°, and detonates at a higher temperature. It is insoluble in water, but is dissolved easily by ether, benzene, or hot alcohol.

Diazo-amidobenzene does not readily unite with acids, though a chloroplatinate is obtainable. By nitric acid containing nitrous acid, diazo-amidobenzene is converted into diazobenzene nitrate; by strong hydrochloric acid into aniline hydrochloride, phenol, and nitrogen.

Amidoazo-Compounds.

When diazo-amidobenzene is heated in the dry state in presence of aniline and a little aniline hydrochloride, it undergoes a molecular transformation into a m i d o - a z o b e n z e n e or *aniline yellow*, identical with the body obtained by the reduction of nitro-azobenzene:[1]—$C_6H_5.N_2.NH(C_6H_5) = C_6H_5.N_2.C_6H_4(NH_2)$.

It is important to notice the leading differences between diazoamidobenzene and the metameric body amido-azobenzene. Thus the latter is a well-defined base, which on heating with an acid forms a salt which gives a red color to the aqueous solution; while the former when similarly treated is decomposed into phenol, nitrogen, and aniline (hydrochloride).

If (instead of aniline) a solution of meta-phenylenediamine[2] be

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[1] Diazobenzene chloride reacts with the secondary monamines to form diazoamido-substitution products. Thus with diethylamine, d i e t h y l d i a z o-a m i d o-b e n z e n e results: — $C_6H_5.N_2.Cl + HN(C_2H_5)_2 = C_6H_5.N_2.N(C_2H_5)_2 + HCl$. With a tertiary monamine a different reaction results, a substituted amidoazo-compound being formed. Thus diazobenzene chloride and dimethylaniline give the hydrochloride of dimethyl-amido-azobenzene $C_6H_5.N_2.Cl + C_6H_5N(CH_3)_2 = C_6H_5.N_2.C_6H_4.N(CH_3)_2.HCl$. The primary amines of naphthalene react in a similar manner.

[2] META-PHENYLENEDIAMINE, $C_6H_4(NH_2)_2$, may be obtained by the reduction of d i n i t r o b e n z e n e, $C_6H_4(NO_2)_2$, produced by treating benzene with a mixture of fuming nitric and strong sulphuric acids. 250 grammes of iron filings are shaken in a flask with 15 c.c. of hydrochloric acid, 50 grammes of dinitrobenzene are then thoroughly mixed with the filings, and boiling water added. A violent action occurs, which must be maintained by the gradual addition of another 50 grammes of dinitrobenzene, and the reaction is completed by boiling the liquid for a few minutes. The solution is then made alkaline by adding lime, filtered, and the phenylenediamine extracted from the filtrate by agitation with ether.

Phenylenediamine melts at 63° and boils at 287° C. It is sparingly soluble in water, but very soluble in alcohol and ether. Its solutions are alkaline, and it behaves as a di-acid base, the hydrochloride being $C_6H_4(NH_2)_2,2HCl$.

Ortho- and para-phenylenediamine do not react with diazobenzene compounds.

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poured into a very dilute solution of diazobenzene chloride, the hydrochloride of d i a m i d o - a z o b e n z e n e or *chrysoïdine* separates as a sparingly soluble precipitate:—$C_6H_5.N_2.Cl + C_6H_4(NH_2)$ $+ C_6H_5.N_2.C_6H_3(NH_2)_2HCl$.

On adding potassium nitrite to a solution of a neutral salt of meta-phenylenediamine, a brown precipitate (or in very dilute solutions, a brown coloration) is produced, which is due to the formation of t r i a m i d o - a z o b e n z e n e or *phenylene-brown*, C_6H_4-$(NH_2).N_2.C_6H_3(NH_2)_2$.

Thus the three amido-azobenzenes are related to each other in the following manner:—

AMIDO-AZOBENZENE, or aniline-yellow base, $C_6H_5.N_2.C_6H_4(NH_2)$.
DIAMIDO-AZOBENZENE, or chrysoidine base, $C_6H_5.N_2.C_6H_3(NH_2)_2$.
TRIAMIDO-AZOBENZENE, or phenyl- } $C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2$.
   ene-brown base,

Diamidoazo Compounds. When an acid radical or benzylidine is substituted for the amido group in the para-amidoazo bodies, subsequent nitration will cause the nitro group to enter the other aromatic nucleus in the para-position to the azo group. By reduction and splitting off of these nitro compounds para-diamidoazo bodies are obtained. By this method diamidoazo-toluol may be produced. It melts at 100°, is readily soluble in dilute acids, alcohol and benzol, rather soluble in hot water, giving nice crystals on cooling.

Aniline Yellow, $C_6H_5.N_2.C_6H_4.NH_2,HCl$, also called *spirit-yellow*, is the hydrochloride of amido-azobenzene, and can be obtained by mixing dilute aqueous solutions of azobenzene chloride and aniline. In the pure state it forms bluish-violet, lustrous needles, soluble in water with a yellow color turned to a fine red by acids. In strong sulphuric acid it dissolves with a brown color, becoming red on dilution. On heating the aqueous solution of aniline yellow, the free base is precipitated. Free amido-azobenzene is also completely precipitated from its salts by ammonia, and may then be taken up by agitation with ether. In the pure state it forms yellow crystals, which melt at 120° and volatilize unchanged. It is insoluble in water, but soluble in alcohol. Acid solutions dye silk red, the salt itself being taken up, but on washing with water the salt is decomposed and the base imparts a yellow color to the fibre. Aniline yellow is not fast, and easily volatilizes when the fibre is steamed. Hence it is not now used as

a dye, but forms the starting point in the manufacture of other aniline colors and of indulines.

Chrysoïdine,[1] $C_6H_5.N_2.C_6H_3(NH_2)_2.HCl$, is the hydrochloride of diamido-azobenzene (page 146). It is formed when an aqueous solution of metaphenylenediamine is poured into a very dilute solution of diazobenzene chloride. It usually occurs in the form of a reddish-brown crystalline powder, or blackish-green or dark violet crystals having a metallic reflex. It is soluble in boiling water and absolute alcohol. The hot concentrated solution forms a gelatinous blood-red mass on cooling. The brown or orange-colored aqueous solution is turned red by excess of hydrochloric acid, dyes wool orange-yellow, and gives with alkalies a bright yellow precipitate of the free base, melting at 117.5° C., and slightly soluble in water, readily in alcohol and ether. Strong sulphuric acid dissolves chrysoïdine with reddish-brown or orange color, which turns almost scarlet on heating (distinction from phosphine), and cherry-red on dilution. Chrysoïdine is used in combination with safranine to produce a scarlet[2] on mordanted cotton.

DIMETHYL-AMIDO-AZOBENZENE, $(C_6H_5.N_2.C_6H_4.N(CH_3)_2$, sometimes called *butter yellow*, is the dimethyl-derivative of aniline yellow. When pure, it crystallizes in small yellow plates, melting at 115° C., and its hydrochloride forms purple-red hair-like needles. It is insoluble in water, but dissolves with red coloration in hydrochloric acid, from which sodium hydrate throws down an orange yellow precipitate of the base; soluble in strong sulphuric acid with yellow color, turning red on dilution. Its alcoholic solution has been recommended by B. F i s c h e r (*Analyst*, x. 152) as an indicator in alkalimetry, in preference to methyl-orange, which is the ammonium salt of its sulphonic acid. It is chiefly used for coloring butter and oils.

PHENYL-AMIDO-AZOBENZENE, $C_6H_5.N_2.C_6H_4.NH(C_6H_5)$, is produced by acting on diphenylamine by diazobenzene chloride in alcoholic solution. It crystallizes in golden yellow prisms, soluble

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[1] Chrysoidine has the peculiar property of precipitating cholera bacilli quantitatively from solutions in which they are held in suspension. Other azo-compounds do not possess this property. As a disinfectant in this respect it occupies a position half-way between mercuric chloride and phenol.

[2] A mixture of chrysoidine and safranine is sometimes sold as C o t t o n S c a r l e t. C h r y s o i d i n e R is a homologue of the above derived from ortho-toluidine and metatolylenediamine.

in alcohol, ether, benzene, and ligroin, but insoluble in water; melting point 82° C. Acids color the alcoholic solution violet and precipitate the salt as grey crystals. Concentrated sulphuric acid dissolves it with a green color, which is changed to violet on dilution with water. Amyl nitrite converts it into a nitrosamine melting at 119.5° C. By reducing agents it is converted into aniline and para-amidodiphenylamine.

Hydroxy-Azo-Compounds.

When potassium phenate is added to a solution of diazobenzene nitrate, h y d r o x y - a z o b e n z e n e is produced according to the following reaction:—

$$C_6H_5.N:N.NO_3 + C_6H_5.OK = C_6H_5.N:N.C_6H_4.OH + KNO_3.$$
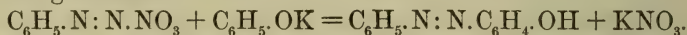
The same body results from the reaction of amido-azobenzene with nitrous acid, or when azobenzene-sulphonic acid is fused with caustic potash. The corresponding derivatives of resorcinol, naphthol, etc., can be obtained by similar means.

HYDROXY-AZOBENZENE, or PHENOL-AZO-BENZENE, $C_6H_5.N_2.C_6H_4.$ OH, is best prepared by dissolving 30 parts of potassium nitrite in 4000 parts of water, and adding the solution to 20 parts of phenol and 20 of aniline nitrate dissolved in 2000 parts of cold water. The liquid is filtered after a few hours, and the precipitate treated with ammonia, which leaves resinous matter undissolved. The hydroxy-azobenzene is precipitated from the filtered liquid by hydrochloric acid.

Hydroxy-azobenzene crystallizes in yellowish-red rhombic prisms, melting at 152–154° C. It is only slightly soluble in water, but readily in alcohol. It has marked acid characters, is readily soluble in alkalies, and forms a series of metallic salts. The silver compound is a yellow precipitate which detonates at 100°.

Hydroxy-azobenzene is not employed as a coloring matter, but its s u l p h o n a t e has been used under the name of *Tropœolin Y.*

META-DIHYDROXY-AZOBENZENE, or RESORCINOL-AZO-BENZENE, $C_6H_5.N_2.C_6H_3(OH)_2.$ This body is formed by the action of diazobenzene nitrate on an alkaline solution of resorcinol. It forms red needles, melts at 168°, and is readily soluble in alcohol. In commerce it occurs as a brown powder under the name of *Soudan G.* It is partly soluble in hot water, with yellow color, the solution giving a bright brown precipitate with hydrochloric acid. In alkalies it is soluble with brown color, and with concentrated sulphuric acid it yields a yellowish-brown solution, giving a brown

precipitate on dilution.   It is used for coloring oils and varnishes.

The acid potassium and sodium salts of the s u l p h o n i c a c i d of resorcinol-azobenzene occur in commerce under the name of *Chyrsoïn, Tropæolin O* or *R*, etc.

BETANAPHTHOL-AZO-BENZENE, $C_6H_5.N_2.C_{10}H_6.OH\beta$.   Obtained by the action of diazobenzene nitrate on an alkaline solution of beta-naphthol.   Under the name of *Soudan I*, it occurs in commerce as a brick-red powder, insoluble in water, but soluble in alcohol with yellow color.   Concentrated sulphuric acid dissolves it with magenta-red color; and on dilution the solution gives an orange-yellow precipitate.   It is chiefly employed for coloring oils and varnishes.

The sodium salt of the corresponding s u l p h o n i c a c i d forms the coloring matter known as *Crocein orange* or *ponceau 4 BG*.

SOUDAN II is homologous with Soudan I, being produced by the action of a diazoxylene compound on betanaphthol.[1]   It is also called *Red B*, and is used for coloring oils and varnishes.   It is insoluble in water, but soluble in alcohol with an orange color.   It dissolves in concentrated sulphuric acid to a magenta-red solution, which gives a pale yellow precipitate on dilution with water.

ALPHANAPHTHOL-AZO-NAPHTHALENE, $C_{10}H_7.N_2.C_{10}H_6.OH^a$, occurs in commerce under the name of *Soudan brown* or *Pigment brown*. It is an insoluble brown powder, dissolving sparingly in dilute alkalies.   In concentrated sulphuric acid it dissolves with blue coloration, a brown precipitate being produced on dilution with water. It is soluble in alcohol, and is used for coloring soaps and oils.

CARMINAPHTHA is a coloring matter isomeric with Soudan brown, being produced by the reaction of diazotized betanaphthylamine on an alkaline solution of betanaphthol.   It is a reddish-brown powder, insoluble in water, but soluble in alcohol.   It dissolves in strong sulphuric acid to form a magenta-red solution, which on dilution gives a brownish-red precipitate.

Sulphonated Azo-Compounds.

The amido- and hydroxy-derivatives of azobenzene and its analogues have marked dyeing properties, but owing to their sparing solubility in water it is found convenient to sulphonate them. This is effected by treatment with fuming sulphuric acid; or, instead of sulphonating after diazotizing, which lessens the yield of coloring matter, the aniline or other amine is first sulphonated and

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[1] Soudan III is the commercial name of a coloring matter of the tetrazo-class.

then diazotized, and the diazo-sulphonic acid formed is then caused to react with other amines or phenols, according to the character of the dye required. In this manner s u l p h a n i l i c a c i d, $C_6H_4(SO_3H)^p.NH_2$,[1] and n a p h t h i o n i c a c i d, $C_{10}H_6(SO_3H)^a.NH_2{}^a$, form the starting points of important series of azo-coloring matters. When diazotized, these two bodies are converted respectively into d i a z o b e n z e n e - s u l p h o n i c a c i d (page 144) and d i a z o n a p h t h a l e n e - s u l p h o n i c a c i d. By the reaction of the former of these with aniline, *acid yellow* is obtained, while with dimethyl-aniline *helianthin* is the product. With phenol in alkaline solution, the sodium salt of phenyl-diazobenzene-sulphonic acid is obtained, known commercially as *tropæolin Y;* with resorcinol the analogous *chrysoïn* or *tropæolin O* results; alpha-naphthol gives Poirrier's *orange I*, or *tropæolin OOO No. 1;* while betanaphthol yields Poirrier's *orange II* or *mandarin.*

In the case of the foregoing colors it is always the amine which is sulphonated. On the other hand, if the phenol be first sulphonated, and then caused to react on a diazotized chloride, bodies are obtained which are isomeric with the former, but possess very different coloring and other properties. *Crocein orange* (page 149) is a dye of this class.
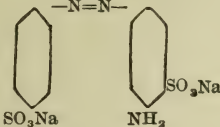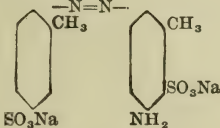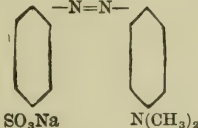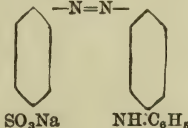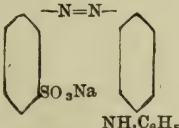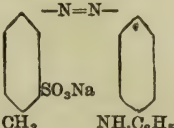
Tropœolins. Yellow and Orange Sulphonated Azo-Dyes.

When diazobenzene-sulphonic acid (obtained by mixing solutions of sulphanilic acid and sodium nitrite) acts on amides or alkaline solutions of phenols, a series of coloring matters are obtained, ranging from yellow to deep orange, and called t r o p æ o - l i n s, because the shades of color they produce resemble those of the flowers of *Tropæolum majus.* They usually occur in commerce as sodium salts, and are distinguished according to their shades, tropæolin Y being the most yellow, and then tropæolins O, OO, and so on, as the shade becomes redder.[2] The shade of color becomes redder by the substitution of toluene, xylene, or cumene for benzene, and hence some of the higher homologues are considered in the section on "azo-reds."
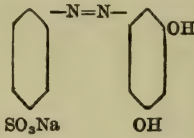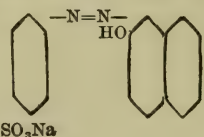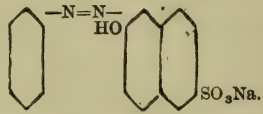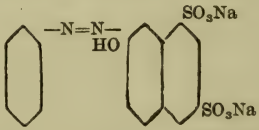
The following is a list of the yellow and orange dyes of this class of commercial importance:—

[1] See Vol. III, pt. II, p. 49.

[2] A valuable paper by O. Mühlhäuser, on the manufacture of the orange azo-dyes, will be found in the *Jour. Soc. Dyers and Colorists*, iii. 135.

COMMERCIAL NAME.	CHEMICAL NAME OR NATURE.	FORMULA.	REMARKS.
Amido-Azo-Dyes. Acid yellow. Fast yellow. Acid yellow G. Fast yellow G. Fast yellow extra. New yellow L. Jaune acide.	Mixture of sodium amidoazobenzene disulphonate with sodium amido-azo-benzene mono-sulphonate.	—N=N— SO_3Na NH_2 SO_3Na	. . .
Fast yellow R. Fast yellow. Yellow W.	Sodium salt of amidoazotoluene disulphonic acid.	—N=N— CH_3 CH_3 SO_3Na SO_3Na NH_2	. . .
Helianthin. Methyl orange Poirrier's orange III. Dimethylaniline orange. Tropæolin D.	Sodium salt of parasulphobenzene-azodimethylaniline.	—N=N— SO_3Na $N(CH_3)_2$	. . .
Diphenylamine yellow. Orange IV. Tropæolin OO. Orange M. Fast yellow. Orange GS. New Yellow. Orange W. Acid yellow D.[1]	K or Na salt of diphenylamine-azo-benzene-para-sulphonic acid.	—N=N— SO_3Na $NH.C_6H_5$	. . .
Metanil yellow.[2] Orange MN. Tropæolin G.	Na salt of diphenylamine-azo-benzene-meta-sulphonic acid.	—N=N— SO_3Na $NH.C_6H_5$	. . .
Fast yellow N. Curcumein. Yellow OO.	Na salt of diphenylamine-azo-toluene-sulphonic acid.	—N=N— SO_3Na CH_3 $NH.C_6H_5$	Two isomers occur.

[1] *Brilliant yellow S* is the sodium sulphonate of orange IV.

[2] The sulphonic acid of metanil yellow is known as *metanil yellow S*.

COMMERCIAL NAME.	CHEMICAL NAME OR NATURE.	FORMULA.	REMARKS.
Amido-Azo-Dyes. Azoflavine. Azo-yellow. Azo-acid-yellow. Indian yellow.[1]	A mixture of nitro - deriva - tives of di-phenylamine.		
Hydxoxy-Azo-Dyes. Tropæolin R or O.[2] Resorcin yellow. Chrysoïn. Chryseolin. Yellow T. Gold yellow. Acme yellow.	Na salt of Resorcinol-azobenzene-para-sulphonic acid.	—N=N—⟨ ⟩OH ; SO₃Na　OH	Seldom met with.
Tropæolin OOO No. 2.[3] Orange II. β-Naphthol orange. Mandarin G. Chrysaurein. Gold orange. Orange extra. Atlas orange.	Na salt of Betanaphthol-azobenzene-para-sulpho-nic acid.	—N=N— HO ; SO₃Na	
Crocein orange. Brilliant orange. Orange GRx. Ponceau 4GB.[4]	Na salt of Benzene-azo-betanaphthol-sulphonic acid.	—N=N— HO ; SO₃Na.	
Orange G. Orange yellow Orange GG.[5]	Na salt of Benzene-azo-betanaphthol-disulphonic acid G.	SO₃Na ; —N=N— HO ; SO₃Na	Homologues are red.

[1] By the action of nitric acid on diphenylamine yellow, *Curcumein (new yellow, citronin)* is first formed; then by further action azo-acid yellow.

[2] *Tropæolin Y,* the sodium salt of phenol-azo-benzene-para-sulphonic acid is obsolete.

[3] *Orange I, Tropæolin OOO No. 1, Sulphanaphthol Orange, Naphthol Orange* or *Orange B,* the corresponding dye from α-naphthol, is obsolete. *Orange R, Mandarin G R, Orange T,* or *Kermesin Orange* and *Orange 2 R,* are homologues of *Orange II,* being derived from toluidine and xylidine respectively, instead of from aniline.

[4] *Tropæolin OOOO,* the corresponding dye from α-naphthol, is obsolete. *Orange G T,* or *Orange RN* and *Scarlet GR* or *Scarlet R* are homologues prepared respectively from toluidine and xylidine instead of anilin.

[5] *Ponceau 2 G* is isomeric with Orange G, and *Ponceau G T* and *R T* are homologues from toluidine.

COMMERCIAL NAME.	CHEMICAL NAME OR NATURE.	FORMULA.	REMARKS.
Hydroxy-Azo-Dyes. Orange No. 3 (not Helianthin).	Na salt of Meta-nitro-benzene-azo-betanaphthol-disulphonic acid.		Not often met with.
Alizarin yellow GG.	Meta nitro-benzene-azo-salicylic acid.	$C_6H_4 \begin{cases} (3)NO_2 \\ (1)N=N-(1)C_6H_3 \begin{cases} (4)OH \\ (3)CO_2H \end{cases} \end{cases}$	Though requiring a mordant, is not a true alizarine.
Alizarin yellow R.	Para nitro-benzene-azo-salicylic acid.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N=N-(1)C_6H_3 \begin{cases} (4)OH \\ (3)CO_2H \end{cases} \end{cases}$	
Lancaster yellow.	Dinitro-phenol-azo-phenol.	$C_6H_2 \begin{cases} (NO_2)_2 \\ OH \\ N=N-C_6H_4.OH \end{cases}$	Obsolete.
Milling yellow.	Sodium salt of sulphonaphthalene-azo-salicylic acid.	$C_{10}H_6 \begin{cases} SO_3Na \\ N=N(4)C_6H_3 \begin{cases} (1)OH \\ (2)CO_2H \end{cases} \end{cases}$	Used with chrome mordant.
Yellow-fast-to-soap.	Sodium salt of meta-carboxylbenzene-azodiphenyl-amine.	$C_6H_4 \begin{cases} (3)CO_2Na \\ (1)N=N-(1)C_6H_4(4)NH.C_6H_5 \end{cases}$	Dyed from a soap bath.
Clayton yellow. Thiazol yellow. Turmerin.	Sodium salt of the diazo-amido compound of dehydrothio-toluidine sulphonic acid.	$C_6H_3 \begin{cases} (4)CH_3 \\ (1)N \\ (2)S \end{cases} {>} C(4)C_6H_3 \begin{cases} SO_3Na \\ (1)N \end{cases}$ $C_6H_3 \begin{cases} (2)S \\ (1)N \\ (4)CH_3 \end{cases} {>} C(4)C_6H_3 \begin{cases} NH.N \\ SO_3Na \end{cases}$	
Oriol yellow. Alkali yellow. Cotton yellow R.	Sodium salt of primuline-azo-salicylic acid.	$P-N=N-(4)C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ (P=radical of primuline.)	
Persian yellow.	Nitro-compound of para-toluene-azo-salicylic acid.	$C_6H_3 \begin{cases} CH_3 \\ N=N-C_6H_2 \begin{cases} OH \\ CO_2H \\ NO_2(?) \end{cases} \end{cases}$	
Narcein.	Sodium bi-sulphite compound of para-sulpho-ben-zene-azobeta-naphthol.	$C_6H_4 \begin{cases} (4)SO_3Na \\ (1)NH-N(SO_3Na)-(1)C_{10}H_6(2)OH \end{cases}$	

The following table shows the general character and reactions of the more important orange and yellow sulphonated azo-dyes:—

Commercial Name of Dye.	Character of Solid Dye of Commerce.	Color of Aqueous Solution.	Behavior of Aqueous Solution with Reagents.				Reaction of Solid Dye with Sulphuric Acid.		Products Formed on Reduction with Zinc and Hydrochloric Acid.
			On adding Caustic Soda.	On adding Hydrochloric Acid.	With Barium Chloride.	With Calcium Chloride.	With Strong Acid.	On Dilution with Water.	
AMIDO-AZO-DYES.									
Acid yellow.	Yellow powder.	Yellow.	No change.	Yellow ppt. soluble in excess with reddish-yellow or cherry-red color.	Precipitate.	No precipitate.	Brownish-yellow.	Orange-yellow.	Sulphanilic acid and para-diamido-benzene.
Fast yellow R.	Brownish-yellow powder.	Yellow.	No change.	Magenta-red.	··	··	Yellowish-brown.	Magenta-red.	··
Helianthin; Methyl orange.	Orange-yellow powder.	Orange.	No change; orange ppt.	Red-violet; crystalline ppt. in strong solution.	··	··	Yellow or reddish brown.	Carmine-red.	Sulphanilic acid and dimethyl-para-di-amido-benzene.
Diphenyl-amine yellow.	Orange-yellow crystalline powder.	Yellow.	No change.	Red color; or violet precipitate.	Precipitate.	Precipitate.	Violet.	Reddish-violet with slate-grey precipitate.	Sulphanilic acid and para-amido-di-phenylamine.
Metanil yellow.	Brownish-yellow powder.	Orange.	No change.	Precipitate and crimson-red color.	Sparingly soluble ppt.	Sparingly soluble ppt.	Dirty violet.	Magenta-red.	Amidobenzene-meta-sulphonic acid and para-amido-di-phenyl-amine.
Orange N.	Orange-red sparingly soluble.	Yellow.	Yellow ppt.	Violet or steel-blue ppt.	Yellow crystalline ppt.	··	Bluish-green.	Violet with steel-blue ppt.	··

COMMERCIAL NAME OF DYE.	CHARACTER OF SOLID DYE OF COMMERCE.	COLOR OF AQUEOUS SOLUTION.	BEHAVIOR OF AQUEOUS SOLUTION WITH REAGENTS.				REACTION OF SOLID DYE WITH SULPHURIC ACID.		PRODUCTS FORMED ON REDUCTION WITH ZINC AND HYDROCHLORIC ACID.
			On adding Caustic Soda.	On adding Hydrochloric Acid.	With Barium Chloride.	With Calcium Chloride.	With Strong Acid.	On Dilution with Water.	
AMIDO-AZO-DYES. Azoflavine.	Ochre-yellow powder.	Yellow.	Yellow-brown color.	Reddish-violet or brownish.	Sparingly soluble crystal-line ppt.	No precipitate.	Reddish-violet.	Red and brown yel-low ppt.	• •
HYDROXY-AZO-DYES. Tropaeolin Y.	Brownish-yellow powder.	Reddish-yellow.	No change.	No change.	• •	• •	Brownish-yellow.	No change.	Sulphanilic acid and amido-phenol.
Resorcin yellow; Chrysoïn.	Brown powder.	Orange.	Reddish-brown.	No change.	• •	• •	Orange-yellow.	Reddish-yellow.	Sulphanilic acid and amido-resorcinol.
Orange I; α-Naphthol yellow.	Brick-red powder.	Orange.	Red-brown.	Yellow-brown flakes.	• •	Red precipi-tate.	Violet.	Brown precip-itate; follow-ed by orange solution.	Sulphanilic acid and amido-alphanaph-thol.
Orange II; β-Naphthol yellow; Mandarin.	Yellow-red powder.	Orange.	Changed to brown-red.	Brownish-yel-low ppt. in strong solu-tions only.	Sparingly soluble crystal-line pre-cipitate.	Yellow ppt., becoming dirty red and crystalline on boiling with water.	Carmine-red.	Brownish-yel-low precipi-tate.	Sulphanilic acid and amido-betanaph-thol.
Crocein orange.	• •	• •	• •	Yellow-brown precipitate.	• •	• •	Orange-yellow.	Yellow-brown precipitate.	Aniline, amido-beta-naphthol, and sul-phuric acid.
Orange G.	Yellowish-red pow-der.	Reddish-yellow.	Changed to brown.	Not changed.	• •	Orange scales.	Orange yellow.	Unchanged.	Aniline, amido-beta-naphthol, and sul-phuric acid.

Commercial Name of Dye.	Character of Solid Dye of Commerce.	Color of Aqueous Solution.	Behavior of Aqueous Solution with Reagents.				Reaction of Solid Dye with Sulphuric Acid.		Products formed on Reduction with Zinc and Hydrochloric Acid.
			On adding Caustic Soda.	On adding Hydrochloric Acid.	With Barium Chloride.	With Calcium Chloride.	With Strong Acid.	On Dilution with Water.	
HYDROXY-AZO-DYES. Orange No. 3 (not Helianthin).	Red-brown powder.	Reddish-yellow.	Changed to yellowish-brown.	Orange-yellow precipitate, soluble in much water.	..	..	Orange-yellow.	Orange ppt., soluble in excess of water to a yellow solution.	Nitraniline, amido-beta-naphthol, and sulphuric acid.
Alizarin yellow G G.	Yellow paste or powder.	Yellow.	Orange yellow solution.	Yellow ppt.	Unchanged.	Unchanged.	Orange-yellow.	Yellow ppt.	..
Alizarin yellow R.	Brown paste.	Orange.	Blood-red solution.	Yellow ppt.	Yellow-brown residue.	Yellow-brown residue.	Orange-red.	Brown ppt.	..
Lancaster yellow.	Dark-brown crystals.	Brownish-yellow.	Yellow-red.	..	..	..	Reddish-yellow.	..	..
Milling yellow.	Yellow powder.	Yellow.	Orange.	Brown ppt.	..	..	Yellowish-red.	..	..
Yellow-fast-to-soap.	Brown paste.	Yellow-brown.	No change.	Reddish-violet.	..	..	Violet.	Ruby-red.	..
Clayton yellow.	Yellow powder.	Yellow.	Orange ppt.	Orange ppt.	..	..	Brownish-yellow.	Paler.	..
Oriol yellow.	Red powder.	Orange.	Redder.	Yellow ppt.	..	..	Scarlet.	Yellow ppt.	..
Persian yellow.	Brownish-yellow powder.	Yellow.	Orange.	Brown ppt.	..	..	Orange.	Brown ppt.	..
Narceïn.	Orange powder.	Yellow.	Brownish-red.	No change.	..	..	Yellowish-brown.	Evolves SO_2 when warmed.	..

The best way of effecting the reduction of the yellow or orange azo-dyes is to warm the solution of the coloring matter with zinc-dust and hydrochloric acid, the action in an ammoniacal solution being somewhat slow. Reduction with ammonium sulphide, in the manner described on page 116, may sometimes be conveniently employed.

The following is a detailed description of some of the more important sulphonated azo-yellows and oranges:—

Acid Yellow. Fast Yellow.[1] (See page 154.) When aniline is heated with fuming sulphuric acid, p a r a - a m i d o b e n z e n e - s u l p h o n i c a c i d (sulphanilic acid) is obtained. On dissolving this in a large quantity of water and adding sodium nitrite and hydrochloric acid, d i a z o b e n z e n e - s u l p h o n i c acid results. On treating the solution with aniline, removing the excess of the latter by hydrochloric acid, and adding common salt, the a m i d o - a z o b e n z e n e - s u l p h o n i c a c i d, $C_6H_4(SO_3H).N_2.C_6H_4(NH_2)$, separates as a yellow precipitate, and forms the *solid yellow S* of commerce.[2] It is also prepared by heating aniline yellow with from three to four parts of fuming sulphuric acid. The commercial product known as *acid yellow* is prepared by dissolving the the sulphonic acid in sodium carbonate and precipitating the solution by common salt. The potassium salt is also employed. Acid yellow is a yellow powder, readily forming a yellow solution in water, but only sparingly soluble in alcohol. On acidulating the aqueous solution with hydrochloric acid the free sulphonic acid is thrown down in the form of minute needles, soluble in excess of hydrochloric acid with reddish-yellow color, appearing crimson in thin layers, the change being probably due to the formation of a hydrochloride. Acid yellow is not precipitated by ammonia or fixed alkalies, nor by basic lead acetate. It is precipitated by barium chloride, but not by calcium chloride. Sulphuric acid dissolves the solid dye with a yellow color. Zinc-dust decolorizes the solution, but the filtered liquid recovers its yellow color on exposure to the air.

Acid yellow is used for dyeing wool and silk, but it is not often used alone for pure yellow colors; for although it is comparatively

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[1] *Acid yellow G* (gelb) is a derivative of amido-azobenzene. The homologue from amido-azotoluene is somewhat more orange in shade, and is known as *acid yellow R*, or *fast yellow R*. The name *fast yellow* is also applied to diphenylamine yellow and to a body of the formula, $C_6H_4(COOH).N_2.C_6H_4.NH(C_6H_5)$.

[2] Much of the acid yellow of commerce contains more or less of a disulphonate.

fast and will stand steaming, it is not sufficiently bright, and is sensitive to acids.   As its shade does not incline toward the red, it is well adapted for use in compound colors, such as olive- and moss-green, and browns, where it replaces the natural yellow dye-stuffs, it being as fast to light as the best of the latter.   Acid yellow is also used extensively for the manufacture of diazo-colors.

Fast Yellow R is produced in a manner analogous to acid yellow, by sulphonating amidoazotoluene.   It is a brownish-yellow powder, giving a yellow solution with water.   Its application is similar to acid yellow, but its shade is orange-yellow.

Methyl Orange. HELIANTHIN. Poirrier's Tropæolin D. Orange III.[1] Gold Orange. Mandarin Orange. (Page 154.) These names, among others, are applied to the ammonium or sodium salt of d i-m e t h y l - a m i d o - a z o b e n z e n e - s u l p h o n i c a c i d, or para-sulphobenzene-azodimethylaniline, $C_6H_4(SO_3H)(4).N_2(1).C_6H_3.-N(CH_3)_2(4)$, a body produced by the action of dimethyl-aniline on diazobenzene-sulphonic acid.   Helianthin forms an orange-yellow powder, readily soluble in hot water, but only sparingly in alcohol.   The aqueous solution is orange-yellow, and is not precipitated by alkalies.   On adding hydrochloric acid to a hot, concentrated aqueous solution, the free sulphonic acid is precipitated in microscopic needles, which soon change to small, strongly lustrous plates or prisms having a violet reflection.   Concentrated sulphuric acid dissolves helianthin with reddish or yellowish brown color, the solution appearing yellow in thin layers.   On copious dilution, the liquid becomes a splendid red.   With most reagents, helianthin behaves similarly to acid yellow, but basic acetate of lead throws down the whole of the coloring matter as an orange-yellow precipitate.   Sodium chloride or magnesium sulphate added to a dilute solution of helianthin precipitates a coloring matter in microscopic crystals.

Silk and wool when immersed in an acid solution of helianthin are dyed a fiery orange.   The dyed fibre is turned red by hydrochloric acid, and yellow by strong sulphuric acid, but alkalies produce no change.

Methyl-orange now receives extensive application as an indicator in alkalimetry.   The yellow color which it imparts to aqueous and alcoholic liquids is changed to red by a strong acid, but is wholly

[1] *Orange III* is a name which is also applied to a coloring matter patented by Roussin and Poirrier, and having the constitution of a sodium salt of metanitro-benzene-azobetanaphthol-disulphonic acid (see page 156).

unaffected by weak acids. Thus the titration of sodium carbonate by sulphuric or hydrochloric acid can be effected in the cold, if helianthin be used as an indicator of neutrality, the carbonic acid liberated having no effect on the coloring matter.[1] Methylorange may be employed for the titration of aniline, toluidine, and quinoline, as these give an alkaline reaction, whereas their salts are neutral. It can also be used in the estimating of such alkaloids as morphine, strychnine, quinine, cinchonidine, and atropine.

The following acids are wholly unindicated by methyl-orange, and hence the base of their salts can be titrated by hydrochloric acid in the cold just as though the acids were absent:—carbonic, hydrocyanic, hydrosulphuric, arsenious, silicic, boric, oleic, stearic, palmitic, carbolic, etc. With oxalic, acetic, butyric, succinic, lactic, tartaric, and citric acids inaccurate results are obtained, but sulphuric, hydrochloric, and nitric acids give sharp end-reactions. The following salts are neutral to methyl-orange, and hence their formation is an end-point of titrations in which they are produced:—$Na_2S_2O_3$, $KaHSO_3$, NaH_2PO_4, $CaH_4(PO_4)_2$, NaH_2AsO_4, $K_2Cr_2O_7$. Methyl-orange can be used to detect free acid in alum, ferrous sulphate, cupric chloride, etc. The earthy carbonates in hard water (which occasion the so-called "temporary hardness") may be at once determined by titrating the water with a mineral acid and methyl-orange.[2]

Ethyl-orange is preferred by Wieland to its lower homologue as an indicator of neutrality. Lacmoïd, cochineal, congo-red, and dimethyl-amidoazobenzene behave much like helianthin.

Methyl-orange is not applicable as an indicator in presence of nitrous acid or nitrites, which compounds decompose it.

Diphenylamine Yellow. This coloring matter, the *Tropæolin OO*[3] of M. Witt, and Poirrier's *orange MN*, also known as *gold-*

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[1] The delicacy and applications of methyl-orange and other indicators in volumetric analysis have been described in a series of valuable papers by R. T. T h o m p s o n (*Jour. Soc. Chem. Ind.*).

[2] A mixture of methyl orange and phenolphthalein solutions serves as an excellent neutrality indicator; the neutral point being indicated by a lemon-yellow color, and the slightest excess of either acid or alkali give a deep pink or a fine red respectively.

[3] A nitro-derivative occurs in commerce under the same name. When the solution is reduced with zinc and hydrochloric acid and filtered, the filter-paper is stained brown. The solid substance deflagrates and gives off yellow vapors when heated on platinum foil (see Azoflavine).

orange, acid-yellow D, diphenylamine-orange, fast-yellow, and *Manchester-yellow* (Perkin) is a phenylated acid yellow. The free sulphonic acid is obtained by the action of diazobenzene-sulphonic acid on diphenylamine. The diphenylamine is added in the form of powder to the solution of the diazobenzene sulphonic acid (diazotized sulphanilic acid) and the mixture agitated for some hours, till the reaction is complete. It forms steel-grey needles, very sparingly soluble in water with pink coloration. It is a powerful acid, forming well-defined salts, almost all of which are remarkable for their insolubility.[1] The commercial dye is a potassium or sodium salt, and forms an orange-yellow crystalline powder, or golden-yellow dichroïc crystals, often arranged in the form of a fan. It is readily soluble in hot water, but only very sparingly in cold water or alcohol. Very small quantities of mineral salts precipitate it from its solutions. The hot aqueous solution is yellow, and unchanged by caustic alkalies, but turned reddish-violet by hydrochloric acid, and on cooling a violet precipitate is formed. Calcium and barium chlorides give yellow crystalline precipitates. In strong sulphuric acid, the dye dissolves with violet color, becoming redder on adding water, while a slate-grey precipitate is produced.

When reduced with an acid solution of stannous chloride, tropæolin OO yields sulphanilic acid and para-amido-diphenylamine, which may be extracted by ether after adding excess of caustic soda to the solution.

Diphenylamine yellow gives a fine golden-yellow on silk or wool. The fibre is turned blue-violet by sulphuric and red-violet by hydrochloric acid.

Tropæolin OO may be substituted for methyl-orange as an indicator in alkalimetry, a faint trace of strong mineral acid turning the dilute solution red, while carbonic and other weak acids have no effect.[2]

Metanil yellow is isomeric with diphenylamine yellow. *Brilliant yellow, acid yellow OO, yellow N,* and *orange N* are names given to the homologues of diphenylamine yellow. Two distinct isomers are met with.

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[1] The t r i m e t h y l a m i n e s a l t is the only one easily soluble in cold water. The a n i l i n e s a l t when treated with an excess of boiling aniline is suddenly transformed into i n d u l i n e, $C_{18}H_{15}N_3$, a blue coloring matter isomeric with phenyl-amido-azobenzene.

[2] Tropæolin OOO, or naphthol-azobenzene-sulphonic acid, behaves in a precisely opposite manner, being turned red by a trace of alkali.

Orange II is produced by the action of betanaphthol on the diazo-compound of sulphanilic acid. It is not sensitive to either acids or alkalies, and is extensively employed in wool-dyeing, both as a self-color and in compound shades.

Luteoline is a higher homologue from diazotized metaxylidine-sulphonic acid. It is now nearly obsolete, but occurred as a difficultly soluble orange-yellow powder. The hot aqueous solution deposits crystals on cooling, gives an orange-yellow precipitate with soda, and a violet precipitate with hydrochloric acid. In strong sulphuric acid the dye dissolves with yellowish-green color, a violet precipitate being formed on dilution. With calcium chloride, luteoline gives an orange precipitate, which on boiling becomes red and crystalline.

Azoflavine is produced by the nitration of diphenylamine yellow, and is a mixture of more or less mono-, di- and tri-nitrodiphenylamine with the body $C_6H_4(SO_3H).N_2.C_6H_4.NH(C_6H_4NO_2)$. It forms an ochre-yellow powder, soluble with difficulty in cold but readily in hot water. The aqueous solution is yellow, changing to brownish on addition of hydrochloric acid. When reduced in ammoniacal solution it becomes yellow. Barium chloride gives a slightly soluble crystalline precipitate, but no change results with calcium chloride. The solid dye dissolves in strong sulphuric acid with magenta-red color, changing to yellowish-red, with a yellowish-brown precipitate, on dilution with water. When heated on platinum foil the dye forms "Pharaoh's serpents," and gives off yellow vapors. After reduction and filtration, brown spots are produced on the filter paper.

Curcumeïn, Azoflavine S or *2, Azo-yellow, Citronine B* or *2 B, Indian Yellow,* and *New Yellow,* are names applied to varieties of azoflavine. They must not be confounded with the *citronin* of Brooke, Simpson, and Spiller, or with *curcumin S* or *sun-yellow,* which is the sodium salt of azo-oxystilbene-disulphonic acid.

Azo-Reds.

The scarlets, ponceaus, and clarets derived from azobenzene and its allies are among the most important of the coloring matters from coal-tar. The ready production and fast character of crocein scarlet and allied dyes seem not unlikely to cause the extinction of the cochineal industry. The general method of producing the azo-reds may be exemplified by the process of preparing *xylidine-red.* For this purpose, x y l i d i n e, $C_6H_3(CH_3)_2NH_2$, is dissolved in

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twice the quantity of hydrochloric acid necessary to combine with it, and after copious dilution of the liquid with ice-cold water a solution of the calculated quantity of sodium nitrite is gradually added with constant stirring. The resultant (neutral) solution of diazoxylene chloride is allowed to flow into a dilute ammoniacal solution of sodium betanaphtholdisulphonate, when ammonium chloride and *xylidine-scarlet* or s o d i u m x y l e n e - a z o b e t a - n a p h t h o l - a l p h a - d i s u l p h o n a t e are produced:—

$$C_6H_3(CH_3)_2.N_2.Cl + C_{10}H_5(SO_3Na)_2.OH\beta + NH_3$$

$$= NH_4Cl + C_6H_3(CH_3)_2.N_2.C_{10}H_4(SO_3Na)_2.OH\beta.$$
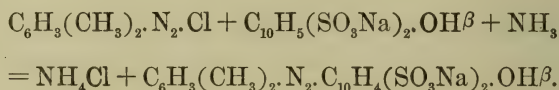
After standing, the liquid is boiled, filtered from resinous matter, and the coloring matter precipitated by addition of salt.[1]

The following table contains a description of some of the more important azo-dyes of which xylidine-scarlet is the type. The commercial names of the dyes are often confusing, the same chemical compound receiving different names from its several makers, while, on the other hand, identical or very similar names are commercially used to distinguish dyes of distinctly different chemical nature.

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[1] Owing to the facility with which diazo-compounds react with phenoloids and their sulphonic acids in alkaline solution, it is possible to produce azo-dyes directly on the fibre by immersing the goods alternately or simultaneously in a solution of naphthol and the diazo salt, and then developing the color in an alkaline bath. The method is especially applicable to cotton, which does not take up ready-formed azo-dyes. Another method of operating is to employ the nitrite required for diazotizing in the form of an ammonium salt, when on heating the goods this is decomposed in the presence of the phenoloid and amine, and thus produces the azo-color *in situ*. The coloring matter known as *primuline* can be diazotized in the fabric, and on subsequently immersing the goods in an alkaline solution of resorcinol or naphthol the azo-dye is developed. Another method of utilizing this diazo-reaction is to develop on the fibre a diazo color by coupling it with diazotized paranitraniline in an alkaline bath. Prumiline, the diamine nitrazol colors, and some other derivatives of benzidine are capable of undergoing this so-called "coupling process." The peculiarity of this method is that the developer and not the dyestuff is diazotized. The property possessed by the hydroxyazo-dyes of forming soluble compounds with acid sulphite of sodium which are decomposed by heat is also utilized. *Narceine*, $C_6H_4(SO_3Na).NH.N(NaSO_3).C_{10}H_6.OH\beta$, is a substance of this class. It is a compound of orange II with acid sodium sulphite, and has been used in calico printing. It is decomposed on steaming, sulphurous acid being liberated and orange II reformed.

The letters appended to the commercial names of dyestuffs are usually indicative of the particular shade, R referring to red (roth), G to yellow (gelb), and B to blue (blau); 2R, etc., means a deeper shade of red than a simple R.   At times other letters are employed for the purpose of trade distinctions, and refer to some private nomenclature of the manufacturing firm.   The method of writing the formulæ has been selected with the view of indicating as far as possible the structure of the molecule and the relative positions of the substituting groups in the benzene and naphthalene nuclei; the large figures in brackets placed before the different substituting groups refer to these positions in the nuclei, as shown by the following diagrams:

COMMERCIAL NAME.	FORMULA.	REMARKS.	CHARACTER OF DYE.
Archil substitute. Naphthionic Red.	$C_6H_4\begin{Bmatrix}(4)NO_2\\(1)N{=}N(2)C_{10}H_5\begin{Bmatrix}(1)NH_2\\(4)SO_3Na\end{Bmatrix}\end{Bmatrix}$	From naphthionic acid.	Brown paste; red-brown solution.
Cochineal Scarlet 2 R.	$C_6H_4(CH_3){-}N{=}N{-}C_{10}H_5\begin{Bmatrix}(1)OH\\(5)SO_3Na\end{Bmatrix}$	From C acid. Homologue is scarlet 4 R.	Cinnabar-red powder, soluble in hot water to yellow-red solution.
Scarlet G T.	$C_6H_4(CH_3){-}N{=}N{-}(1)C_{10}H_5\begin{Bmatrix}(2)OH\\(6)\ SO_3Na\end{Bmatrix}$	From S acid. Homologue is scarlet G R.	Scarlet powder; solution orange-yellow.
Azococcin 2 R.	$C_6H_3(CH_3)_2{-}N{=}N{-}(2)C_{10}H_5\begin{Bmatrix}(1)OH\\(4)SO_3Na\end{Bmatrix}$	From Neville's acid.	Brown-red powder, difficultly soluble; bronzy crystals on cooling.
Wool Scarlet R.	$C_6H_3(CH_3)_2{-}N{=}N{-}(2)C_{10}H_4\begin{Bmatrix}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{Bmatrix}$	From R salt.	Brown-red powder; solution yellowish-red.
Ponceau 2 R. Scarlet R. Xylidine Scarlet.	$C_6H_3(CH_3)_2{-}N{=}N{-}(1)C_{10}H_4\begin{Bmatrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{Bmatrix}$	From R Salt. Isomers of yellower shade from G salt. Ponceau G, and scarlet G.	Scarlet powder; easily soluble; red solution.
Ponceau 2 G. Scarlet 2 G and 2 R.	$C_6H_5{-}N{=}N{-}(1)C_{10}H_4\begin{Bmatrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{Bmatrix}$	From G salt. Isomers from R salt.	Brown-red powder. Fine red solution.
Ponceau 3 R.[1]	$C_6H_2\begin{Bmatrix}(5)CH_3\\(4)CH_3\\(2)CH_3\\(1)N{=}N{-}C_{10}H_4\begin{Bmatrix}OH\ \beta\\(SO_3Na)_2\end{Bmatrix}\end{Bmatrix}$	From R salt.	Dark red powder; solution cherry-red.
Anisol Red. Anisidine Ponceau.	$C_6H_4\begin{Bmatrix}(1)OCH_3\\(2)N{=}N{-}(1)C_{10}H_5\begin{Bmatrix}(2)OH\\(6)SO_3Na\end{Bmatrix}\end{Bmatrix}$	From R salt.	Brownish-red powder; solution cherry-red.
Phenatol Red. Coccinin. Coccin.	$C_6H_4\begin{Bmatrix}(2)OC_2H_5\\(1)N{=}N{-}C_{10}H_4\begin{Bmatrix}OH\ \beta\\(SO_3Na)_2\end{Bmatrix}\end{Bmatrix}$	From R salt.	Fine red solution.
Coccinin B.	$C_6H_3\begin{Bmatrix}(1)CH_3\\(4)OCH_3\\(3)N{=}N{-}C_{10}H_4\begin{Bmatrix}OH\ \beta\\(SO_3Na)_2\end{Bmatrix}\end{Bmatrix}$	From R salt.	Dark red powder; solution cherry-red.
Crystal Ponceau 6 R.	$C_{10}H_7(1){-}N{=}N(1)C_{10}H_4\begin{Bmatrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{Bmatrix}$	From γ acid.	Red-brown glittering crystals; solution deep red.
Fast Brown N; Azo Brown O; Napthylamine Brown; Chrome Brown R O.	$C_{10}H_6\begin{Bmatrix}(4)SO_3Na\\(1)N{=}N{-}(4)C_{10}H_6(1)OH\end{Bmatrix}$	From naphthionic acid.	Dark brown powder; solution reddish-brown.

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[1] There is also a *Ponceau 3 R* which is the sodium salt of ethyldimethyl-benzene-azobetanaphthol-disulphonic acid.

REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		PRODUCTS OF REDUCTION WITH ZINC AND AMMONIA.	OTHER CHARACTERS.
With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.		
Precipitate soluble in water.	Precipitate.	Magenta-red.	Brown-red ppt.	Nitraniline and diamido-naphthalene sulphonic acid.	. . .
Orange coloration.	Red flakes.	Magenta-red.	Red flakes.	Toluidine and amido-a-naphthol sulphonic acid.	. . .
Brown-red coloration.	Brown oily drops.	Magenta-red.	Oily drops.	Toluidine and amido-β-naphthol sulphonic acid.	. . .
Brown-yellow color; no ppt.	Brownish-red flakes.	Magenta-red.	Brown-red precipitate.	Xylidine and amido-a-naphthol sulphonic acid.	. . .
Yellow-red color.	Bluish-red coloration.	Cherry-red.	Red solution.	Xylidine and amido-a-naphthol disulphonic acid.	. . .
No precipitate.	No change.	Red.	Brown precipitate.	Amido-β-naphthol disulphonic acid and xylidine.	$BaCl_2$ and $CaCl_2$, amorphous precipitates.
No change.	No change.	Eosin-red.	Yellow-red color.	Amido-β-naphthol disulphonic acid and cumidine.	$BaCl_2$ and $CaCl_2$, precipitates appearing slowly.
Yellow precipitate.	No change.	Cherry-red.	Cherry-red.	Amido-β-naphthol disulphonic acid and ethyl-xylidine.	. . .
Yellowish-red.	No change.	Magenta-red.	Cherry-red.	Amido-β-naphthol disulphonic acid and anisidine.	. . .
Brownish coloration.	. . .	Magenta-red.	Red.	Amido-β-naphthol disulphonic acid and phenatidine.	$BaCl_2$, brown, sparingly soluble precipitate. $CaCl_2$ red precipitate gradually.
Brown ppt. soluble to red-brown solution.	Darkened.	Magenta-or cherry-red.	Cherry-red.	Amido-β-naphthol disulphonic and methyl anisidine.	$BaCl_2$, brown ppt. $CaCl_2$, red precipitate formed gradually
Bright brown.	Darkened; with excess, brown crystalline ppt.	Violet.	Scarlet.	. . .	. . .
No change.	Brown ppt.	Blue.	Brown ppt.	Amido-a-naphthol and a-naphthol-amine sulphonic acid.	. . .

Commercial Name.	Formula.	Remarks.	Character of Dye.
Roccelline. Fast Red A. Rubidine. Cerasine.	$C_{10}H_6 \begin{cases} (4)SO_3Na \\ (1)N{=}N{-}(1)C_{10}H_6(2)OH \end{cases}$	From naphthionic acid.	Solution reddish-brown, forms brown jelly when rapidly cooled.
Fast Red C. Azorubin S. Carmoisin.	$C_{10}H_6 \begin{cases} (4)SO_3Na \\ (1)N{=}N{-}(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic acid and Neville's acid.	Brown powder; magenta-red solution.
New Coccin. Brilliant Ponceau.	$C_{10}H_6 \begin{cases} (4)SO_3Na \\ (1)N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)OH \\ (6)SO_3Na \\ (8)SO_3Na \end{cases} \end{cases}$	From naphthionic acid and G salt.	Scarlet-red powder; sparingly soluble.
Fast Red D. Amaranth.	$C_{10}H_6 \begin{cases} (4)SO_3Na \\ (1)N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From naphthionic acid and R salt.	Reddish-brown powder; solution magenta-red.
Cochineal. Scarlet G.	$C_6H_5{-}N{=}N{-}(2)C_{10}H_5 \begin{cases} (1)OH \\ (5)SO_3Na \end{cases}$	From L acid.	Brick-red powder; yellow solution.
Tropæolin 0000.	$C_6H_5{-}N{=}N{-}(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases}$	From N W acid.	Reddish-brown powder; orange solution.
Brown N P and N P J.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N{=}N{-}(1)C_6H_2 \begin{cases} (2)OH \\ (3)OH \\ (4)OH \end{cases} \end{cases}$	From diazotized paranitraniline and pyrogallol.	Brown paste.
Archil Substitute G.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \end{cases}$	From paranitraniline and beta-naphthylamine.	Brown powder; red solution.
Archil Substitute 3 V N.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N{=}N{-}C_{10}H_5 \begin{cases} (1)NH_2 \\ (5)SO_3Na \end{cases} \end{cases}$	From L acid.	Brown powder; red solution.
Archil Substitute Extra. Apollo Red.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N{=}N{-}C_{10}H_4 \begin{cases} NH_2 \\ SO_3Na \end{cases} \end{cases}$	From paranitraniline and alpha-naphthylamine-disulphonic acid.	Brown powder; red solution.
Ponceau R T.	$C_6H_4 \begin{cases} CH_3 \\ N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From R acid.	Red powder; orange solution.
Cochineal. Scarlet 4 R.	$C_6H_3(CH_3)_2{-}N{=}N{-}C_{10}H_5 \begin{cases} (1)OH \\ (5)SO_3Na \end{cases}$	From L acid.	Red powder; slightly soluble.
Scarlet G R. Scarlet R.	$C_6H_3(CH_3)_2{-}N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases}$	From S acid.	Red powder; orange solution.
Palatine. Scarlet.	$C_6H_3(CH_3)_2{-}N{=}N{-}C_{10}H_4 \begin{cases} OH \\ (SO_3Na)_2 \end{cases}$	From naphthol-disulphonic acid.	Red powder; red solution.
Ponceau G. Scarlet G.	$C_6H_3(CH_3)_2{-}N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)OH \\ (6)SO_3Na \\ (8)SO_3Na \end{cases}$	From G acid.	Red powder; red solution.
Ponceau 3 R.	$C_6H_2 \begin{cases} C_2H_5 \\ (CH_3)_2 \\ N{=}N{-}C_{10}H_4 \begin{cases} OH\beta \\ (SO_3Na)_2 \end{cases} \end{cases}$	.	Red powder; red solution.
Azo-eosin.	$C_6H_3 \begin{cases} (2)OCH_3 \\ (1)N{=}N{-}(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.	Red powder; red solution.

REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		PRODUCTS OF REDUCTION WITH ZINC AND AMMONIA.	OTHER CHARACTERS.
With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.		
Darkened.	Yellow-brown ppt.	Violet.	Yellow-brown ppt.	Amido-a-naphthalene sulphonic acid, and amido-β-naphthol.	Na_2CO_3 in strong solution gives pale brown crystals.
Becomes yellow	Brown jelly.	Bluish-violet.	Magenta-red.	a-naphthylamine sulphonic acid and amido-a-naphthol sulphonic acid.	$CaCl_2$, red crystalline precipitate.
Brown.	No change.	Magenta-red.	Yellow red.	a-naphthylamine sulphonic acid and amido-β-naphthol disulphonic acid.	. .
Becomes dark.	No change.	Violet.	Magenta-red.	. .	. .
Orange.	Thick ppt.	Cherry-red.	Red ppt.	. .	. .
Orange.	Orange ppt.	Magenta-red.	No change.	. .	Obsolete.
. .	. .	. .	. .	. .	Is dyed on mordanted wool.
Brown ppt.	Brown ppt.	Red.	Brown ppt.	. .	. .
Brown.	Bluish ppt.	Red.	No change.	. .	. .
Brown ppt.	Crimson.	Crimson.	No change.	. .	. .
Yellow.	No change.	Red.	Orange.	. .	. .
Yellowish-red.	Brown ppt.	Magenta-red.	Red ppt.	. .	. .
No change.	Brown ppt.	Red.	Red ppt.	. .	. .
Yellower.	Brown ppt.	Purple.	Brown ppt.	. .	Soluble in alcohol.
No change.	No change.	Red.	Orange.	. .	. .
Yellow ppt.	No change.	Red.	No change.	. .	. .
Yellowish.	Brown ppt.	Red.	Red ppt.	. .	Slightly soluble in alcohol.

Commercial Name.	Formula.	Remarks.
Cresol Red.	$C_6H_3\begin{cases}(1)CH_3\\(2)OC_2H_5\\N=N-C_{10}H_4\begin{cases}OH\,\beta\\(SO_3Na)_2\end{cases}\end{cases}$	From R acid.
Orcelline. Deep Red.	$C_6H_2\begin{cases}OH\\(NO_2)_2\\N=N-C_6H_3(OH)_2\end{cases}$	From Picramic acid and Resorcinol.
Buffalo Rubine.	$C_{10}H_7(1)N=N-C_{10}H_4\begin{cases}(a)OH\\(SO_3Na)_2\end{cases}$	From Schoellkopf acid.
Fast Red B T.	$C_{10}H_7(1)N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}$	From S acid.
Naphthorubin.	$C_{10}H_7(1)N=N-C_{10}H_4\begin{cases}OH\\(SO_3Na)_2\end{cases}$	From Gürcke and Rudolf's acid.
Fast Red B. Bordeaux B.	$C_{10}H_7(1)N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}$	From R acid.
Palatine Red.	$C_{10}H_7(1)N=N-C_{10}H_4\begin{cases}OH\\(SO_3Na)_2\end{cases}$	$\cdot\ \cdot$
Thiorubine.	$C_6H_3\begin{cases}(1)N\\(2)S\\(4)CH_3\end{cases}{>}C(1)C_6H_4(4)N=N-C_{10}H_4\begin{cases}OH\,\beta\\(SO_3Na)_2\end{cases}$	From R acid.
Erika B.	$C_6H_2\begin{cases}(1)CH_3\\(3)CH_3\\(5)S\\(6)N\end{cases}{>}C(1)C_6H_3\begin{cases}(4)N=N-C_{10}H_4\begin{cases}(1)OH\\(3)SO_3Na\\(8)SO_3Na\end{cases}\\(3)CH_3\end{cases}$	From ε-acid.
Crocein 3 B X.	$C_{10}H_6\begin{cases}(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(8)SO_3Na\end{cases}\end{cases}$	From B acid.
Fast Red E. Fast Red.	$C_{10}H_6\begin{cases}(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}$	From S acid.
Scarlet 6 R. Ponceau 6 R.	$C_{10}H_6\begin{cases}(4)SO_3Na\\(1)N=N-C_{10}H_3\begin{cases}OH\,\beta\\(SO_3Na)_3\end{cases}\end{cases}$	From trisulphonic acid.
Acid Ponceau.	$C_{10}H_6\begin{cases}SO_3Na\\N=N-(1)C_{10}H_6(2)OH\end{cases}$	From a and γ naphthylamines.
Fast Brown 3 B.	$C_6H_4\begin{cases}(6)SO_3Na\\(2)N=N-(4)C_{10}H_6(1)OH\end{cases}$	$\cdot\ \cdot$
Orange Red I. Double Brilliant Scarlet G.	$C_{10}H_6\begin{cases}(6)SO_3Na\\(2)N=N-(1)C_{10}H_6(2)OH\end{cases}$	$\cdot\ \cdot$
Brilliant Ponceau 4 R. Double Scarlet Extra S. Double Brilliant Scarlet 3 R.	$C_{10}H_6\begin{cases}(6)SO_3Na\\(2)N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid.
Pyrotine R R O.	$C_{10}H_6\begin{cases}(5)SO_3Na\\(2)N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid.

CHARACTER OF DYE.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red powder; red solution.	Brown pp.	Darkened.	Red.	No change.	Obsolete.
Brown paste; red solution.	No change.	Brown pp.	Brown.	Brown pp.	Soluble in alcohol.
Brown powder; bluish-red solution.	No change.	No change.	Blue.	Purple.	. .
Red powder; red solution.	Brown.	Brown pp.	Violet.	Violet pp.	Slightly soluble in alcohol.
Brown powder; purple solution.	Orange.	No change.	Violet.	Red.	Obsolete.
Brown powder; purple solution.	Yellow.	No change.	Blue.	Violet.	. .
Blue powder; purple solution.	Yellower.	Brown pp.	Blue.	Brown pp.	. .
Brown powder; purple solution.	Bluer.	Brown pp.	Purple.	Brown pp.	Obsolete.
Brown powder; red solution.	Violet pp.	Red pp.	Red.	Red pp.	Soluble in alcohol.
Red powder; orange solution.	Brown.	No change.	Violet.	Orange.	. .
Brown powder; red solution.	Brown.	No change.	Violet.	Red.	. .
Brown powder; purple solution.	Brown.	No change.	Violet.	Magenta-red.	. .
Red powder; slightly soluble.	Browner.	Brown pp.	Violet.	Brown pp.	Soluble in hot water.
Brown powder; brown solution.	Red.	Violet.	Blue.	Violet pp.	. .
Brown powder; red solution.	Brown pp.	Brown pp.	Bluish-red.	Red pp.	. .
Brown powder; orange solution.	No change.	Brown pp.	Bluish-red.	Scarlet.	. .
Brown powder; orange solution.	Yellower.	Bluer.	Bluish-red.	Red.	. .

COMMERCIAL NAME.	FORMULA.	REMARKS.
Clayton Cloth Red.	$C_6H_3 \begin{Bmatrix} (1)N \\ (2)S \\ (4)CH_3 \end{Bmatrix} C(1)C_6H_4 \begin{Bmatrix} SO_3NH_4 \\ (4)N=N-(1)C_{10}H_6(2)OH \end{Bmatrix}$	From β-naphthol.
Alkali Brown.	$P-N=N-(1)C_6H_3 \begin{Bmatrix} (2)NH_2 \\ (4)NH_2 \end{Bmatrix}$ (P=primuline radical.)	··
Atlas Red.	$P-N=N-(1)C_6H_2 \begin{Bmatrix} (3)CH_3 \\ (4)NH_2 \\ (6)NH_2 \end{Bmatrix}$	··
Terra Cotta R.	$C_6H_5-N=N-C_6H_2 \begin{Bmatrix} OH \\ CO_2H \\ NO_2 \end{Bmatrix}$	··
Azo-fuchsine B.	$C_6H_4 \begin{Bmatrix} CH_3 \\ N=N-C_{10}H_4 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (8)OH \\ (4)SO_3Na \end{Bmatrix}$	From Schoellkopf's acid.
Azo-fuchsine G.	$C_6H_4 \begin{Bmatrix} (4)SO_3Na \\ (1)N=N-C_{10}H_4 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (8)OH \\ (4)SO_3Na \end{Bmatrix}$	From Schoellkopf's acid.
Diamond yellow G.	$C_6H_4 \begin{Bmatrix} (3)CO_2Na \\ (1)N=N-(4)C_6H_3 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (2)CO_2Na \end{Bmatrix}$	··
Diamond yellow R.	$C_6H_4 \begin{Bmatrix} (2)CO_2Na \\ (1)N=N-(4)C_6H_3 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (2)CO_2Na \end{Bmatrix}$	··
Roxamine.	$C_{10}H_6 \begin{Bmatrix} (4)SO_3Na \\ (1)N=N-(1)C_{10}H_5 \end{Bmatrix} \begin{Bmatrix} (2)OH \\ (7)OH \end{Bmatrix}$	··
Chromotrop 2 R.	$C_6H_5N=N(2)C_{10}H_3 \begin{Bmatrix} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{Bmatrix}$	From chromotrop acid.
Chromotrop 2 B.	$C_6H_4 \begin{Bmatrix} NO_2 \\ N=N(2)C_{10}H_3 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{Bmatrix}$	From paranitraniline and chromotrop acid.
Chromotrop 10 B.	$C_{10}H_7(a)N=N(2)C_{10}H_3 \begin{Bmatrix} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{Bmatrix}$	From chromotrop acid.
Chromotrop 8 B.	$C_{10}H_6 \begin{Bmatrix} SO_3Na \\ N=N(2)C_{10}H_3 \end{Bmatrix} \begin{Bmatrix} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{Bmatrix}$	From chromotrop and naphthionic acid.
Prager Alizarin yellow G.	$C_6H_4 \begin{Bmatrix} (4)NO_2 \\ (2)N=N-(2)C_6H_2 \end{Bmatrix} \begin{Bmatrix} (3)OH \\ (5)OH \\ (6)CO_2Na \end{Bmatrix}$	From betaresorcyl acid and metanitraniline.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red powder; brown solution.	. .	Red pp.	. .	. .	. .
Brown powder; red solution.	Red pp.	Brown pp.	Violet.	Brown pp.	Soluble in alcohol.
Red powder; brown solution.	. .	Dark pp.	. .	. .	Gives brown shades when diazotized on fibre.
Brown powder; brown solution.	Red.	Brown pp.	Yellow.	Brown pp.	The presence of the NO_2 group is questioned.
Dark brown powder; red solution.	Bluer.	Brown pp.	Violet.	Bluish-red.	. .
Brown powder; red solution.	Bluer.	Yellower.	Violet.	Bluish-red.	. .
Yellow paste; yellow solution.	. .	. .	Orange.	Yellow pp.	More readily soluble in water containing sodium carbonate or acetate.
Brown paste; yellow solution.	. .	. .	Orange.	Yellow pp.	More readily soluble in water containing sodium carbonate or acetate.
Red powder; scarlet solution.	Darker.	No change.	Violet.	. .	Acid dye for wool.
Red powder, magenta-red solution.	No change.	No change.	Violet.	Orange.	Soluble in alcohol. Acid dye for wool.
Red powder; orange solution.	Violet.	Yellower.	Violet.	Orange.	Soluble in alcohol. Acid and chrome dye for wool.
Violet powder; violet solution.	Orange.	No change.	Blue.	Violet pp.	Soluble in alcohol. Acid dye for wool.
Violet powder; violet solution.	No change.	No change.	Blue.	Violet.	Soluble in alcohol. Acid dye for wool.
Yellow powder; yellow solution.	Orange.	Yellow pp.	Yellow.	Yellow pp.	Soluble in alcohol. Chrome dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Prager Alizarin Yellow R.	$C_6H_4 \begin{cases} (5)NO_2 \\ (2)N=N-(2)C_6H_2 \begin{cases} (3)OH \\ (5)OH \\ (6)CO_2Na \end{cases} \end{cases}$	From beta-resorcyl acid and para-nitraniline.
Para-Nitraniline Red.	$C_6H_4 \begin{cases} (4)NO_2 \\ (1)N=N-(1)C_{10}H_6(2)OH \end{cases}$	From para-nitraniline and beta-naphthol.
Wool Violet S.	$C_6H_3 \begin{cases} (1)NO_2 \\ (5)NO_2 \\ (2)N=N-(2)C_6H_5 \begin{cases} (1)SO_3Na \\ (5)N(C_2H_5)_2 \end{cases} \end{cases}$	From dinitraniline.
Victoria Violet 4 B S.	$C_6H_4 \begin{cases} NH_2 \\ N=N-(2)C_{10}H_3 \begin{cases} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From Chromotrop 2 B.
Chromotrop 6 B.	$C_6H_4 \begin{cases} NH.C_2H_3O \\ N=N-(2)C_{10}H_3 \begin{cases} (1)OH \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From Chromotrop acid.
Spirit Yellow R. Yellow Fat Color.	$C_6H_4 \begin{cases} (1)CH_3 \\ (2)N=N=(2)C_6H_3 \begin{cases} (6)CH_3 \\ (5)NH_2 \end{cases} \end{cases}$	From ortho-toluidine.
Chrysoidin R.	$C_6H_4 \begin{cases} (1)CH_3 \\ (2)N=N-(2)C_6H_2 \begin{cases} (1)NH_2 \\ (4)CH_3 \\ (5)NH_2.HCl \end{cases} \end{cases}$	From ortho-toluidine.
Rose de Benzoyl.	$C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \\ (2)N=N-C_{12}H_6 \begin{cases} NH.CO.C_6H_5 \\ (CH_3)_2 \end{cases} \end{cases}$	From N W acid.
Sulphamin Brown A. Naphthine Brown a.	Not determined.	From a-disazonaphthaline.
Azo Turkey Red.	$C_{10}H_7(3)N=N(1)C_{10}H_6(2)OH$	Developed on fibre from beta-naphthylamine and beta-naphthol.
Sulphamin Brown B. Naphthine Brown β.	Not determined.	From β-disazonaphthaline.
Diamond Flavin G.	$C_6H_3 \begin{cases} (3)CO_2H \\ (4)OH \\ (1)N=N-(1)C_6H_4.C_6H_4.(4)OH \end{cases}$	From salicylic acid.
Indoïn Blue R.	Not determined.	From safranine.
Phenoflavin.	$C_6H_4 \begin{cases} (4)SO_3Na \\ (2)N=N(2)C_6H_2 \begin{cases} (1)NH_2 \\ (3)SO_3Na \\ (5)OH \end{cases} \end{cases}$	From metanilic acid.
Fast Red B.	$C_{10}H_6 \begin{cases} SO_3Na \\ N=N-C_{10}H_5 \begin{cases} OH \\ CH_2.C_{10}H_6.OH \end{cases} \end{cases}$	From naphthionic acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Orange powder; orange solution.	Violet.	Orange ppt.	Orange.	Orange ppt.	Soluble in alcohol. Chrome dye for wool.
The dyestuff is made on the fibre.	. .	. .	. .	. .	Ingrain dye for cotton.
Black powder; violet solution.	Violet ppt.	Orange.	Scarlet.	Orange ppt.	Soluble in alcohol. Acid dye for wool.
Green powder; violet solution.	Orange.	Orange.	Violet.	Orange ppt.	Soluble in alcohol. Acid dye for wool.
Brown powder; violet solution.	Yellow.	No change.	Red.	Violet ppt.	Soluble in alcohol. Acid dye for wool.
Yellow lumps; but slightly soluble, melt in boiling water.	. .	Red crystals.	Brown.	Red ppt.	Soluble in hot alcohol. Color for fats, butter, etc.
Violet crystals; red solution.	Yellow ppt.	Brown ppt.	Brown.	Red ppt.	Soluble in alcohol.
Red lumps.	Red.	Violet ppt.	Red.	. .	Direct dye for cotton.
Brown powder; brown solution.	Brown ppt.	No change.	Green.	Brown.	Chrome dye for wool.
. .	. .	. .	. .	. .	Ingrain color.
Brown powder; brown solution.	Brown ppt.	No change.	Violet.	Brown.	Chrome dye for wool.
Brown paste; insoluble.	Orange solution.	No change.	Red.	Brown ppt.	Soluble in alcohol.
Brown paste or powder; violet solution.	Violet ppt.	Blue ppt.	Green.	Violet ppt.	Soluble in alcohol. Direct color for cotton.
Yellow powder; yellow solution.	Orange.	Orange.	Yellow.	. .	Acid dye for wool.
Brown powder; red solution.	Darker.	Brown ppt.	Violet.	Brown ppt.	Acid dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Fast acid scarlet. Fast acid Ponceau.	$C_{10}H_6 \begin{cases} (4)SO_3Na \\ (6)N=N-(1)C_{10}H_6.(2)OH \end{cases}$	From beta-acid.
Chrome yellow D. Anthracene yellow B N. Milling yellow.	$C_{10}H_6 \begin{cases} (6)SO_3Na \\ (2)N=N-(2)C_6H_3 \begin{cases} (4)CO_2H \\ (5)OH \end{cases} \end{cases}$	From salicylic acid.
Crumpsall-yellow.	$C_{10}H_5 \begin{cases} (6)SO_3Na \\ (8)SO_3Na \\ (2)N=N-(2)C_6H_3 \begin{cases} (4)CO_2H \\ (5)OH \end{cases} \end{cases}$	From salicylic acid.
Cotton Orange G.	$P-N=N(2)C_6H \begin{cases} (1)NH_2 \\ (3)SO_3Na \\ (4)SO_3Na \\ (5)NH_2 \end{cases}$ (P=primuline base.)	From diazotized primuline.
Diamond yellow G.	$C_6H_4 \begin{cases} (4)CO_2H \\ (2)N=N(2)C_6H_3 \begin{cases} (4)CO_2H \\ (5)OH \end{cases} \end{cases}$	From salicylic acid.
Chicago Orange.	$CH.C_6H_3 \begin{cases} (1)NO \\ (3)SO_3Na \end{cases}$ $\parallel$ $CH.C_6H_3 \begin{cases} (3)SO_3Na \\ (1)N=N-C_6H_4.C_6H_4.NH_2 \end{cases}$	From Benzidine.
Arnica yellow.	$CH.C_6H_3 \begin{cases} (1)NO \\ (3)SO_3Na \end{cases}$ $\parallel$ $CH.C_6H_3 \begin{cases} (3)SO_3Na \\ (1)N=N-C_6H_4OH \end{cases}$	From para-amidophenol.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red powder; but slightly soluble.	Darker.	Brown pp.	Violet.	Brown pp.	Acid dye for wool.
Yellow powder; orange solution.	Orange pp.	Gray pp.	Orange.	Gray pp.	Chrome dye for wool.
Yellow powder; yellow solution.	Green pp.	Orange pp.	Orange.	Orange.	Soluble in alcohol. Chrome dye for wool.
Brown powder; orange solution.	No change.	Red pp.	Orange.	Red pp.	Direct dye for cotton.
Yellow paste; yellow solution.	. .	. .	Orange.	Yellow pp.	Soluble in alcohol. Chrome dye for wool.
Brown powder; orange solution.	Orange pp.	Brown pp.	Violet.	Brown pp.	Soluble in alcohol. Direct dye for cotton.
Brown powder; brown solution.	Red.	Brown pp.	Violet.	. .	Direct dye for cotton.

The dyes of the class of which xylidine scarlet is the type are very numerous, and are being continually added to. The characters of the dyes are materially dependent on their derivation from alpha- or beta-naphthol, and the exact nature of the isomeric naphthol-sulphonic acids employed also notably affects the color and other properties of the dye. The letters R and G (the initial letters of the words *roth* and *gelb*) appended to the commercial names of the scarlets and other azo-dyes have reference to the sodium salts of the respective isomeric beta-naphtholdisulphonic acids used for their production. "S a l t G" yields the yellow shades, and "s a l t R" the red shades of the azo-dyes they are employed to produce. Similarly, where beta-naphtholmonosulphonic acid is used, the characters of the resultant dyes depend to some extent on the isomer employed, whether "Schäffer's acid," "Bayer's acid," or other modification.[1]

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[1] When betanaphthol is heated with twice its weight of strong sulphuric acid (sp. gr. 1.845) to about 90° C., until completely sulphonated, the chief product is a monosulphonic acid known as S c h ä f f e r ' s a c i d ("acid S"). When betanaphthol is added gradually to twice its weight of strong sulphuric acid (sp. gr. 1.845), taking care that the temperature does not rise above 50° to 60° C., Schäffer's acid and an isomeric acid, b e t a n a p h t h o l - a l p h a s u l p h o n i c a c i d, often known as B a y e r ' s a c i d ("acid B"), are formed in about equal quantity. The use of a temperature of 20° C. for preparing Bayer's acid has been patented. Schäffer's and Bayer's acids may be separated by converting them into sodium salts and treating the dry product with alcohol, in which liquid the salt of betanaphthol-alphasulphonic acid is by far the most readily soluble. Another method of separating Bayer's acid from Schäffer's and another isomeric said to be present is based on the different facility with which the three acids act on certain azo-compounds. Thus by treating the alkaline solution of the mixed sulphonic acids with a properly regulated quantity of tetrazo-diphenol, the unnamed acid and Schäffer's acid are precipitated as claret-colored dyes, while Bayer's acid remains in solution in the requisite purity for the manufacture of crocein scarlet, for which purpose the isomeric acids are not available. A naphthol-sulphonic acid distinct from, and giving shades redder than, either the above acids, is said to be obtainable by a process described in Patent No. 15,781, of 1885 (*Jour. Soc. Dyers, etc.*, ii. 199).

When betanaphthol is heated with three times its weight of concentrated sulphuric acid (1.845 sp. gr.) to 100° or 110° C., it is converted into a mixture of two isomeric d i s u l p h o n i c a c i d s. To separate these, the liquid should be diluted, neutralized with milk of lime, and filtered after allowing sufficient time for the precipitated calcium sulphate to crystallize. The filtrate is treated with sodium carbonate, and the filtered liquid evaporated to dryness. From the mixture of the isomeric sodium salts obtained, "salt G" can be dissolved by alcohol, while "salt R" is left insoluble. According to J. W e t t e r (*Jour. Soc. Chem. Ind.*, iv. 339), the isomeric acids can be separated by treating the solution of their *acid*

Xylidine Red, or SCARLET R,[1] obtained as described on page 164, forms a scarlet-red powder, readily soluble in water or acetic acid, but less so in glycerin or alcohol. Its aqueous solution is unchanged by alkalies or dilute acids, and gives scarlet lakes with the acetates of lead and aluminium. Barium chloride precipitates it more perfectly, even in the presence of acetic acid. Xylidine scarlet dyes animal fibres without a mordant in a slightly acid bath. When fixed by means of a barium salt it withstands the action of boiling water very well. The color does not stand soaping, but is fast in the air, and resists the action of light fairly well, though it fades slowly when exposed to direct sunshine.[2]

Xylidine red and allied colors are frequently adulterated with *dextrin,* which may be separated by treating the sample with sufficient alcohol. Tarry matters are sometimes precipitated on acidulating the solution of the dye with acetic acid.

Fast-Brown N. By the action of alphanaphthol on diazotized naphthionic acid a compound is obtained having a naphthalene nucleus on both sides of the chain, and of the following formula:— $C_{10}H_6(SO_3Na)^a.N_2.C_{10}H_6(OH)^a$. This coloring matter, like others of similar constitution, dyes wool brown in an acid bath. It forms a dark brown powder soluble in water to form a yellowish-brown solution changed to brownish-red by soda and giving a brown precipitate with hydrochloric acid. In strong sulphuric acid the dye dissolves with blue color, a brown precipitate being formed on dilution.

An isomeric coloring matter from alphanaphthol and diazotized

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sodium salts with brine, when salt R crystallizes out, while salt G remains in solution. (The same process is said to be applicable to the separation of Schäffer's and Bayer's monosulphonic acids.) Another b e t a n a p h t h o l - d i s u l p h o n i c a c i d (γ) has been described and patented by Gaus and Hoffman (*Jour. Soc. Chem. Ind.,* iii. 567; iv. 742), and is used for the production of *crystal ponceau 6 R,* by reaction in alkaline solution with diazotized α-naphthylamine.

By the extreme action of fuming sulphuric acid on betanaphthol, a t r i s u l p h o n i c a c i d is obtainable.

The manufacture of sulphonic acids and nitrosulphonic acids from alpha-naphthol has been recently patented by H. C a r o. Other sulphonic acids of alpha- and beta-naphthol and of the naphthylamines have been described and patented.

[1] The commercial Xylidine scarlets are not prepared from chemically pure substances and are mixtures of several very similar azo-compounds. Scarlet 2 G is sometimes added for shading purposes.

[2] The Xylidine scarlets are rapidly replacing cochineal in commerce, owing to their low price and simple method of application.

beta-naphthylamine-sulphonic acid gives a brownish-red solution, turned magenta-red by soda or dilute acids. It is soluble in strong sulphuric acid with blue color, giving a reddish-violet precipitate on dilution.

Other brown coloring matters are described with the tetrazo-dyes.

Secondary Azo-Compounds. Tetrazo-Dyes.

Amido-azobenzene may be regarded as a primary amine, since it contains the group NH_2. When this is attacked by nitrous acid the diazo-reaction occurs, and a d i a z o - a z o b e n z e n e compound is formed:—$C_6H_5.N_2.C_6H_4NH_2HCl + NaNO_2 + HCl = C_6H_5.N_2.C_6H_4.N_2.Cl + NaCl + 2H_2O$. The product contains the —N:N— group in two places, and is called a s e c o n d a r y a z o - or t e t r a z o - c o m p o u n d.[1] By reaction with phenols in presence of alkalies, these tetrazo-compounds yield products of which several have received practical applications, as they usually possess a coloring power superior to that of the azo-dyes of similar color but simpler constitution. They are rendered soluble by sulphonation, the SO_3H group being often introduced into both chains. Thus by diazotizing acid yellow, and acting with the product on sodium betanaphthol-alphasulphonate (Bayer's salt), s o d i u m b e t a n a p h t h o l s u l p h o n a t e - a z o b e n z e n e - a z o b e n z e n e - s u l p h o n a t e of ammonium, or *crocëin scarlet*, is obtained, according to the following equation:—

$$C_6H_4(SO_3H).N:N.C_6H_4.N:N.Cl + C_{10}H_6 \left\{ \begin{matrix} SO_3Na(\alpha) \\ OH(\beta) \end{matrix} \right\} + 3NH_3 =$$
$$NH_4Cl + C_6H_4 \left\{ \begin{matrix} (4)SO_3NH_4) \\ (1)N=N(4)C_6H_4(1)N=N(1)C_{10}H_5 \end{matrix} \left\{ \begin{matrix} (2)OH \\ (8)SO_3Na. \end{matrix} \right. \right.$$
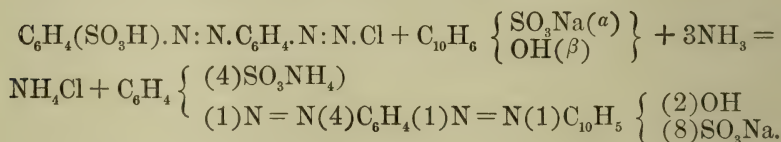
Crocëin Scarlet, 3 B, or *Ponceau 4 RB*, formulated above, is a dye of considerable practical importance. It forms a red-brown powder, soluble in water with a scarlet-red color. The solution is turned violet-red by alkalies, but not precipitated except in very concentrated solutions. With hydrochloric acid it yields a yellowish-brown precipitate. With barium chloride it gives a red pre-

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[1] *Tertiary Azo-Compounds*, containing three —N:N— groups, have been prepared (R. M e l d o l a, *Jour. Chem. Soc.*, xliii. 436), but they have little tinctorial value.

cipitate, becoming dark violet and crystalline on boiling. With calcium chloride the dye gives a flocculent red precipitate, which on boiling the liquid suddenly becomes brown and crystalline. When reduced with zinc in ammoniacal solution crocein scarlet is decolorized. but the liquid acquires a yellow color on exposure to air. The solid dye dissolves in strong sulphuric acid with indigo-blue color, and on dilution a yellow-brown precipitate is formed, soluble in more water to a red solution.

Crocein Scarlet, 7 B, or *Ponceau 6 RB*, is homologous with the last (containing two toluene- instead of benzene-residues) and re-sembles it generally, but after reduction with zinc and ammonia the colorless liquid does not again become yellow on exposure to air. The hot concentrated aqueous solution, when treated with magnesium sulphate and allowed to stand, deposits on cooling long silky needles of the magnesium salt.

PONCEAU S. EXTRA is a disulphonated crocein scarlet:—
$C_6H_4(SO_3Na).N_2.C_6H_3(SO_3Na).N_2.C_{10}H_4(SO_3Na)_2.OH\beta$.

Orseillin 2 B is the metameric compound from alphanaphthol sulphonic acid.

Biebrich Scarlet, *Ponceau 3 R,* or *azobenzene red,* is a mixture of *fast scarlet or double scarlet,* $C_6H_4(SO_3Na).N_2.C_6H_4.N_2.C_{10}H_6.OH\beta$, with the corresponding d i s u l p h o n a t e,

$$C_6H_4 \begin{cases} (4)SO_3Na \\ (1)N = N \end{cases} - C_6H_3 \begin{cases} SO_3Na \\ N = N \end{cases} - (1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na. \end{cases}$$
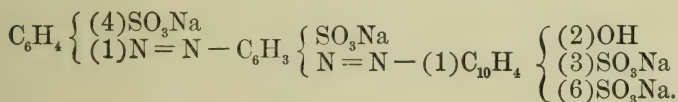
It is a reddish-brown crystalline powder, forming a yellowish-red solution. The hot aqueous solution of Biebrich scarlet becomes gelatinous on cooling. Dilute acids give a flocculent brownish-red precipitate in strong solutions, but the dye is not precipitated by alkalies. (According to some, a brownish-red precipitate). With zinc and ammonia the solution of Biebrich scarlet is decolorized, but on exposure to air the liquid becomes yellow and gives the re-actions of a c i d y e l l o w. The solid dye gives a green solution in strong sulphuric acid, and on adding water, the color changes to blue, then to violet, and lastly a dirty-brown precipitate is formed.

Scarlets 3 B, 3 R, and 4 R are varieties of Biebrich scarlet.

Scarlet S, or *Ponceau SS extra,* is metameric with Biebrich scar-

let, the betanaphthol being sulphonated instead of the amine, thus:—

$$C_6H_5 - N = N - C_6H_4 - N = N - (1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na, \end{cases}$$
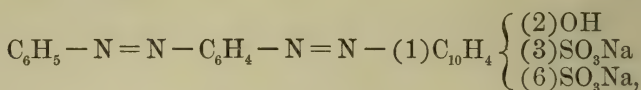
or azobenzene-azobenzene-betanaphthol-disulphonate of sodium. It is a brown powder, soluble in water with magenta-red color. The solution yields a violet precipitate with hydrochloric acid, and is turned reddish-violet by soda.

Brilliant crocëin M is a dye of the same composition prepared with sodium betanaphthol-γ-sulphonic acid instead of salt R. It is a light brown-powder, forming a cherry-red solution, which is turned brown by soda, and gives a brown precipitate with hydrochloric acid.

Azococcin 7 B and Crocëin B are coloring matters from alpha-naphthol analogous to scarlet S. Azococcin 7 B is a difficultly soluble brown powder. The magenta colored solution gives a brownish-red precipitate with hydrochloric acid, and with soda a violet-red precipitate soluble in water. Crocëin B is brown-red, difficultly soluble to a magenta-colored solution which is precipitated violet by hydrochloric acid, and gives a violet coloration with soda. *Archil red* is homologous with scarlet S, containing two xylene- instead of two benzene-residues.

THE TETRAZO-DYES are characterized by their behavior on reduction. With tin or hydrochloric acid, or other acid reducing agent, the decomposition is complete; but when treated with zinc and ammonia only partial decomposition ensues and the decolorized and filtered solution usually acquires a yellow color on exposure to air, the colorless hydrazo-compound formed being oxidized to acid yellow and amido-azobenzene or some allied body. (See below.)

A further distinction between the various red tetrazo-dyes containing a naphthol nucleus is to be found in their behavior when treated in the solid state with strong sulphuric acid, as is shown in the following table:—

Dye.	Color with Sulphuric Acid.		Products of Reduction.	
	With Strong Acid.	On Dilution with Water.	In Alkaline Solution.	In Acid Solution.
A ——— Biebrich scarlet.	Green.	Blue, brown, and brown precipitate.	Amido-β-naphthol and amido-hydra-zobenzene-disul-phonic acid (oxi-dizing with yellow color).	Amido-β-naphthol sulphanilic acid, and para-diamido-benzene-sulphonic acid.
Fast scarlet.	Green.	Blue; then blue-red changing to scarlet.	Amido-β-naphthol para-diamido-ben-zene and amido-hydrazo-benzene sulphonic acid (oxi-dizing with yellow color).	. .
B ——— Scarlet S. Ponceau SS extra.	Violet.	Violet ppt.	Amido-β-naphthol-disulphonic acid and amido-azoben-zene.	Sulphuric acid, amido-β-naphthol, aniline, and para-diamido-benzene.
Brilliant crocein M.	Reddish-violet.	Blue-violet; and red or brown ppt. on further dilution.	. .	. .
Azococcin 7 B.	Bluish-violet.	Brownish-red ppt.	. .	. .
Crocein B.	Violet.	Violet ppt.	. .	. .
C ——— Crocein scar-let 3 B.	Indigo-blue.	Yellow-brown ppt., and then red so-lution.	Amido-β-naphthol-a-sulphonic acid and amido-hydrazoben-zene sulphonic acid (oxidizing to acid yellow).	Sulphuric acid, amido-β-naphthol, sulphanilic acid, and para-diamido-benzene.
Crocein scar-let 7 B.	Blue.	Violet-red.	. .	. .
Orseillin 2 B.	Blue.	Red.	. .	. .
Ponceau S extra.	Blue.	Yellowish-red.	. .	. .

From this table it appears that (A) when the sulphonic group (SO_3H) exists in the benzene nucleus or nuclei only, as in Biebrich scarlet, a green coloration is produced; (B) when the naphthol nucleus is alone sulphonated, as in scarlet S, the dye dissolves in strong sulphuric acid with violet color; while (C) when both the benzene and naphthol or naphthalene residues are sulphonated, as in the croceïn scarlets, a blue coloration is obtained.[1]

SOUDAN III, or Amido-azobenzene-azobetanaphthol. $C_6H_5.N_2.$- $C_6H_4.N_2.C_{10}H_6.OH\beta$. This is the only unsulphonated tetrazo-dye of commercial interest. It forms a brown powder insoluble in water, but soluble in alcohol. It dissolves in concentrated sulphuric acid with bluish-green color, becoming blue on addition of water, and giving a red precipitate on further dilution.

Tetrazo-Browns mostly belong to the class of bodies sometimes called d i s a z o - c o m p o u n d s, the constitution of which is supposed to be somewhat different from that of the ordinary tetrazo-compounds. The following coloring matters of this class occur in commerce:—

Resorcin brown, . $C_6H_2(OH)_2$: $\begin{cases} N:N.C_6H_3(CH_3)_2 \\ N:N.C_6H_4(SO_3Na) \end{cases}$

Fast brown (Bayer), $C_6H_2(OH)_2$: $\begin{cases} N:N.C_{10}H_6(SO_3Na)\beta \\ N:N.C_{10}H_6(SO_3Na)\beta \end{cases}$

Acid brown G, . $C_6H_2(NH_2)_2$: $\begin{cases} N:N.C_6H_5 \\ N:N.C_6H_4(SO_3Na) \end{cases}$

Acid brown R, . $C_6H_2(NH_2)_2$: $\begin{cases} N:N.C_6H_5 \\ N:N.C_{10}H_6(SO_3Na) \end{cases}$

Fast brown G (Tillman's), $C_{10}H_5(OH)^a$: $\begin{cases} N:N.C_6H_4(SO_3Na) \\ N:N.C_6H_4(SO_3Na) \end{cases}$

Fast brown (Meister), $C_{10}H_5(OH)^a$: $\begin{cases} N:N.C_6H_2(CH_3)_2(SO_3Na) \\ N:N.C_6H_2(CH_3)_2(SO_3Na). \end{cases}$

RESORCIN BROWN. $C_6H_3(CH_3)_2.N_2.C_6H_2(OH)_2.N_2.C_6H_4(SO_3Na)$. This compound is one of the few tetrazo-colors not containing a naphthalene nucleus. It is a brown powder, soluble in water to a brown solution which is but slightly changed by soda, but yields a brown precipitate with hydrochloric acid. The solid dye dissolves in strong sulphuric acid with brown color, and on dilution with water a brown precipitate is formed.

[1] AZORUBIN 2 S, produced by reacting on diazotized acid yellow with Neville's a-naphthol-sulphonic acid from napthionic acid (and hence a dye of class C) appears to be an exception to this rule, for it dissolves in sulphuric acid with a green color, becoming blue on dilution.

ACID BROWN G is the type of several similar bodies obtained by introducing an amine residue instead of a phenol residue. It is prepared by the action of diazobenzene chloride on chrysoïdine-sulphonic acid. It dissolves in strong sulphuric acid with reddish-brown color, becoming yellowish on dilution with water.

ACID BROWN R is a similar dye prepared by the action of diazo-tized naphthionic acid on chrysoïdine. It is a brown powder, forming a brown aqueous solution which is unchanged by alkalies, but precipitated brown by acids. In strong sulphuric acid the dye dissolves with a dirty olive color, and on dilution gives first a reddish and then a brown precipitate.

FAST BROWN G is a brown powder, forming a reddish-brown solution. Dilute hydrochloric acid gives a violet precipitate, soluble in excess with a violet color, or in water with a brown color. Alkalies turn the aqueous solution cherry-red. Strong sulphuric acid dissolves the solid dye with a violet color, becoming yellowish-brown on dilution.

FAST BROWN of Meister, Lucius, and Brüning is homologous with the last dye, and forms a dark brown powder soluble in water with a brown color. Alkalies turn the solution reddish-yellow, and dilute acids give a violet precipitate. Strong sulphuric acid dissolves the dye with a violet color, becoming red on dilution. The color produced on wool is a brownish-red.

Phenylene Brown. $C_6H_4 {<}^{N_2-C_6H_3(NH_2)_2}_{N_2-C_6H_3(NH_2)_2} . 2HCl$. This coloring matter, which is also known by the name of *Bismarck brown, vesuvine, Manchester brown, cinnamon brown, leather brown, canelle,* etc., is the hydrochloride of benzene-disazophenylene-diamine.[1] The commercial product forms a dark brown powder always containing more or less common salt, and on solution in water often leaves a residue of insoluble impurities. The aqueous and alcoholic solutions are brown, and do not become gelatinous on cooling, but the liquid is turned red by a large excess of hydrochloric acid, though unchanged by slight excess. This reaction is very characteristic. Ammonia and the fixed alkalies give a voluminous

[1] Phenylene-brown is prepared on a large scale by reducing a known weight of dinitrobenzene with finely-divided iron and a little hydrochloric acid, and then boiling with water and milk of lime. The solution is filtered from the precipitate of iron oxide, and treated in the cold with the quantity of sodium nitrite and dilute hydrochloric acid requisite to react with the meta-phenylenediamine, when the color forms immediately, and is salted out and collected on filters.

brown precipitate of the free base, which is somewhat soluble in boiling water, and more readily in alcohol, and when purified by recrystallization forms small yellowish-red crystals which melt at 137°.   Phenylene-brown dissolves in strong sulphuric acid with reddish-brown coloration, becoming orange-red on dilution.   The aqueous solution gives a brown precipitate with basic lead acetate (distinction from chrysoïdine orange), and is decolorized by treatment with a hydrochloric acid solution of stannous chloride.

Phenylene-brown dyes wool a brownish-orange.   It is much used for dyeing leather.   On cotton it is mordanted with Turkey-red oil, or by tannin and tartar-emetic.

Naphthol Black or Azo-Black contains $C_{10}H_5(SO_3Na)_2.N_2.$ $C_{10}H_6.N_2.C_{10}H_4(OH)\beta(SO_3Na)_2$, and results from the action of salt R on diazotized amido-azonaphthalene-disulphonic acid.   It forms a readily soluble black powder, yielding a dark blue-violet aqueous solution, precipitated red-violet by hydrochloric acid, and giving with alkalies a blue precipitate soluble in much water.   Precipitates are yielded with barium and calcium chlorides, as also by solutions of iron and other heavy metals.   The dye dissolves in strong sulphuric acid with a dark green color becoming blue on dilution.   Naphthol black dyes silk and wool a blue-black in a slightly acid bath.[1]

Wool-Black is a similar dye produced by the reaction of diazotized amido-azobenzene-disulphonic acid on paratolyl-betanaphthylamine, and has the formula, $C_6H_4(SO_3Na).N_2.C_6H_3(SO_3Na).$ $N_2.C_{10}H_6.NH(C_7H_7)\cdot$ It gives a violet precipitate with soda, and a red violet precipitate with hydrochloric acid; and dissolves in strong sulphuric acid with a blue color, yielding a brown precipitate on dilution.   Both wool-black and azo-black are employed as indigo-substitutes in wool-dyeing.   They are fairly fast, and can be applied in the simplest possible manner, namely, by simply immersing the wool in an acid bath of the dye, but the color is apt to bleed in the milling process.

Naphthol Black 3 B has the formula $C_{10}H_5(Na SO_3)_2.N : N.C_{10}$ $H_5(SO_3Na)_2$.   It occurs in the form of a crystalline powder, giving a dark blue solution in water.   In strong sulphuric acid it dissolves with a black color, changing to purple on dilution.   The aqueous solution with hydrochloric acid shows no change, but

---

[1] Naphthol Black is dyed on wool by first boiling the material in an acidulated bath, then adding the dyestuff.   It is very fast against the action of light, acids, and stoving, but only moderately fast to washing.

caustic soda turns it to a bluer color. It is an acid dye for wool, giving deep navy blue shades which are quite fast to acids, alkalies, and light. There are several other naphthol blacks with similar characteristics to the above.

NAPHTHOL BLACK 6 B has the formula $C_{10}H_5(SO_3Na)_2.N:N.$ $C_{10}H_6N:N.C_{10}H_4 \begin{cases} (SO_3Na)_2 \\ OH. \end{cases}$ It differs from the 3 B brand in being soluble in alcohol, and dyeing a redder shade of blue.

NAPHTHOL BLACK 4 R has the same formula as the above, but is made from the β-naphthol-γ-disulphonic acid whereas the former is prepared from β-naphthol-disulphonic acid R.

Naphthylamine Blacks are somewhat similar to the naphthol blacks just described. NAPHTHYLAMINE BLACK D[1] is a combination of amido-azo-naphthalene-disulphonic acid with α-naphthylamine. It dyes the animal fibres from a neutral bath giving black shades with a red tone, which are fairly fast to light and fulling.

Jet Black R is obtained by combining α-naphthylamine with with diazotized benzene sodium disulphonate-azo-naphthylamine. It may be employed as a direct dye on cotton in connection with borax, but only very pale shades are obtained. Animal fibres are dyed from a neutral bath, giving black shades fairly fast to light and milling. JET BLACK G is a very similar dyestuff prepared from the corresponding toluene derivative; it is dyed in the same manner as the former, but gives greener shades of black equally as fast as the R brand.

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[1] Naphthylamine Black has been sold under the name of Alizarin Black, but it is not in any sense an alizarin derivative.

Commercial Name.	Formula.	Remarks.
Fast Brown.	$C_6H_2(CH_3)_2.SO_3Na{-}N{=}N$ $C_6H_2(CH_3)_2.SO_3Na{-}N{=}N$ $>C_{10}H_5OH(a)$	From 2 mols. xylidine sulphonic acid and alpha-naphthol.
Acid Brown R.	$\begin{matrix}NH_2(1)\\NH_2(3)\end{matrix}\}C_6H_2<\begin{matrix}N{=}N{-}C_6H_5\\N{=}N(1)\\NO_3Na(4)\end{matrix}\}C_{10}H_6$	From naphthionic acid + chrysoidine.
Clayton Cotton Brown.	$\begin{matrix}NH_2\\NH_2\end{matrix}\}C_6H_2<\begin{matrix}SO_3Na\\N{=}N(4)\\N{=}N(1)\\SO_3Na(4)\end{matrix}\begin{matrix}CH_3\\C_6H_3(1)C<\!\!\begin{matrix}S(2)\\N(1)\end{matrix}\}C_6H_3\\C_{10}H_6\end{matrix}$	. .
Terra Cotta F.	$\begin{matrix}NH_2\\NH_2\end{matrix}\}C_6H_2<\begin{matrix}N{=}N{-}P\\N{=}N{-}C_{10}H_6.SO_3Na\end{matrix}$ $(P = \text{Primuline radicle.})$	. .
Sudan III.	$C_6H_4\left\{\begin{matrix}N{=}N{-}C_6H_5\\N{=}N{-}C_{10}H_6OH(\beta)\end{matrix}\right.$	. .
Acid Brown G.	$\begin{matrix}NH_2(1)\\NH_2(3)\end{matrix}\}C_6H_2<\begin{matrix}N{=}N{-}C_6H_5\\(4)N{=}N{-}(1)C_6H_4(4)SO_3Na\end{matrix}$	From aniline + chrysoidine.
Resorcin Brown.	$\begin{matrix}HO(1)\\HO(3)\end{matrix}\}C_6H_2<\begin{matrix}(2)N{=}N{-}C_6H_3(CH_3)_2\\(4)N{=}N{-}(1)C_6H_4(4)SO_3Na\end{matrix}$	From xylidine + tropæoline O.
Fast Brown G.	$HO(1)C_{10}H_5\left\{\begin{matrix}(2)N{=}N(1)C_6H_4(4)SO_3Na\\(4)N{=}N(1)C_6H_4(4)SO_3Na\end{matrix}\right.$	From sulphanilic acid + alpha-naphthol.
Fast Brown (Bayer).	$\begin{matrix}HO(1)\\HO(3)\end{matrix}\}C_6H_2\left\{\begin{matrix}(2)N{=}N(1)C_{10}H_6(4)SO_3Na\\(4)N{=}N(1)C_{10}H_6(4)SO_3Na\end{matrix}\right.$	. .
Phenylene Brown. Bismarck Brown. Manchester Brown.	$C_6H_4\left\{\begin{matrix}(1)N{=}N{-}(1)C_6H_3\left\{\begin{matrix}(2)NH_2HCl\\(4)NH_2\end{matrix}\right.\\(3)N{=}N{-}(1)C_6H_3\left\{\begin{matrix}(2)NH_2HCl\\(4)NH_2\end{matrix}\right.\end{matrix}\right.$	From diazotized metaphenylenediamine.
Toluylene Brown.	$C_6H_2\left\{\begin{matrix}N{=}N{-}C_6H_2(NH_2)_2{-}N{=}N{-}C_{10}H_6.SO_3Na\\CH_3\\SO_3Na\\N{=}N{-}C_6H_2(NH_2)_2{-}N{=}N{-}C_{10}H_6.SO_3Na\end{matrix}\right.$	. .
Benzo-Brown G.	$C_6H_4\left\{\begin{matrix}(1)N{=}N{-}(4)C_6H_2\left\{\begin{matrix}(1)NH_2\\(2)N{=}N{-}(1)C_6H_4(4)SO_3Na\\(3)NH_2\end{matrix}\right.\\(3)N{=}N{-}(4)C_6H_2\left\{\begin{matrix}(1)NH_2\\(2)N{=}N{-}(1)C_6H_4(4)SO_3Na\\(3)NH_2\end{matrix}\right.\end{matrix}\right.$	From Bismarck brown.
Benzo-Brown B.	$C_6H_4\left\{\begin{matrix}(1)N{=}N{-}(4)C_6H_2\left\{\begin{matrix}(1)NH_2\\(2)N{=}N{-}(1)C_{10}H_6(4)SO_3Na\\(3)NH_2\end{matrix}\right.\\(3)N{=}N{-}(4)C_6H_2\left\{\begin{matrix}(1)NH_2\\(2)N{=}N{-}(1)C_{10}H_6(4)SO_3Na\\(3)NH_2\end{matrix}\right.\end{matrix}\right.$	From Bismarck brown.

CHARACTER OF OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; brown solution.	Orange.	Violet ppt.	Violet.	Red.	Liable to dye uneven.
Brown powder; brown solution.	No change.	Brown ppt.	Green.	Brown ppt.	. .
Brown powder; brown solution.	No change.	Brown ppt.	Violet.	Brown ppt.	Dyes cotton direct.
Brown powder; brown solution.	No change.	Brown ppt.	Violet.	Brown ppt.	Dyes cotton direct.
Brown powder; insoluble in water, soluble in alcohol.	. .	. .	Green.	Red ppt.	Used for coloring oils and varnishes.
Brown powder; brown solution.	No change.	No change.	Reddish-brown.	Yellowish-brown.	. .
Brown powder; brown solution.	No change.	Brown ppt.	Brown.	Brown ppt.	Fast to light and milling on wool.
Brown powder; brown solution.	Red.	Violet ppt.	Violet.	Yellow.	. .
Brown powder; brown solution.	Red.	Brown ppt.	Violet.	Red.	. .
Brown powder; brown solution.	Brown ppt.	No change.	Brown.	Red.	Converted by reducing agents into phenylene-diamine and tri-amido-benzene.
Dark brown powder; brown solution.	Orange ppt.	Brown ppt.	Violet.	Brown.	Direct cotton dye.
Dark brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct cotton dye.
Dark brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct cotton dye.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Catechu Brown.	$C_6H_4\begin{cases}(1)N=N-(4)C_6H_3\begin{cases}(3)NH_2\\(1)N=N-(4)C_6H_3\begin{cases}(1)NH_2\\(3)NH_2\end{cases}\end{cases}\\(3)N=N-(4)C_6H_3\begin{cases}(3)NH_2\\(1)N=N-(4)C_6H_3\begin{cases}(1)NH_2\\(3)NH_2\end{cases}\end{cases}\end{cases}$	From Bismarck brown.
Direct Brown J.	$C_6H_4\begin{cases}(1)N=N-C_6H_2\begin{cases}(NH_2)_2\\N=N-C_6H_4.CO_2Na\end{cases}\\(3)N=N-C_6H_2\begin{cases}(NH_2)_2\\N=N-C_6H_4.CO_2Na\end{cases}\end{cases}$	From Bismarck brown.
Cloth Red G. Azococcine 7 B.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid.
Croceine B.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(2)C_{10}H_4\begin{cases}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{cases}\end{cases}$	From Sch. acid.
Ponceau R R.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\SO_3Na\end{cases}\end{cases}$	From S acid.
Brilliant Croceine. Cotton Scarlet.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{cases}\end{cases}$	From γ acid.
Ponceau SS extra.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}\end{cases}$	From R acid.
Ponceau 5 R. Erythrin X.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-C_{10}H_3\begin{cases}OH\,\beta\\(SO_3Na)_3\end{cases}\end{cases}$	. .
Croceine 3 B.	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-C_{10}H_4\begin{cases}OH(a)\\(SO_3Na)_2\end{cases}\end{cases}$	From Sch. acid.
Cloth Red G.	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}$	From S acid.
Cloth Red B (Oehler).	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}\end{cases}$	From R acid.
Cloth Red B (Bayer).	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid,
Cloth Red 3 G.	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_5\begin{cases}(2)NH_2\\(6)SO_3Na\end{cases}\end{cases}$	From Br. acid.
Bordeau B X.	$C_6H_2\begin{cases}N=N-C_6H_3(CH_3)_2\\(CH_3)_2\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}$	From S acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; brown solution.	Brown ppt.	Brown ppt.	Brown.	Brown ppt.	Direct cotton dye.
Dark brown powder; brown solution.	No change.	Brown ppt.	Brown.	Brown ppt.	Direct cotton dye.
Brown powder; red solution.	Violet ppt.	Red ppt.	Violet.	Red ppt.	Precipitated from aqueous solution by Glauber's salt.
Red powder; red solution.	Violet.	Violet ppt.	Violet.	Violet ppt.	Acid dye for wool.
Brown powder; red solution.	Violet ppt.	Brown ppt.	Blue.	Brown ppt	Obsolete. Acid dye for wool.
Brown powder; red solution.	Brown.	Brown ppt.	Violet.	Brown ppt.	The finest of the scarlets. Acid dye for wool.
Brown powder; red solution.	Violet.	Violet ppt.	Violet.	Violet ppt.	Acid dye for wool.
Brown powder; red solution.	Brown.	Brown ppt.	Violet.	Red.	Acid dye for wool.
Brown powder; red solution.	Violet.	Violet ppt.	Blue.	Red.	Acid dye for wool.
Brown powder; red solution.	Brown ppt.	Red ppt.	Blue.	Brown ppt.	But sparingly soluble in water. Dyes chromed wool.
Brown powder; red solution.	Red ppt.	Brown.	Blue.	Brown ppt.	Dyes chromed wool.
Red powder; red solution.	Violet.	Red ppt.	Blue.	Red ppt.	Dyes chromed wool.
Red powder; red solution.	No change.	Brown ppt.	Blue.	Red ppt.	Dyes chromed wool.
Brown powder; red solution.	Red ppt.	Red ppt.	Brown.	Brown ppt.	Acid dye for wool. Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Ponceau 4 R B. Croceine Scarlet 3 B.	$C_6H_4 \begin{cases} N=N-(1)C_6H_4(4)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (8)SO_3Na \end{cases} \end{cases}$	From B acid.
Fast Scarlet. Double Scarlet.	$C_6H_4 \begin{cases} N=N-(1)C_6H_4(4)SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{cases}$	. .
Orchil Red A.	$C_6H_2 \begin{cases} N=N-C_6H_3(CH_3)_2 \\ (CH_3)_2 \quad\quad (2)OH \\ N=N-(1)C_{10}H_4 \begin{cases} (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From R acid.
Bordeaux B X.	$C_6H_2 \begin{cases} N=N-C_6H_2 \begin{cases} (CH_3)_2 \\ SO_3Na \end{cases} \\ (CH_3)_2 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases} \end{cases}$	From S acid.
Bordeaux G.	$C_6H_3 \begin{cases} N=N-C_6H_3 \begin{cases} CH_3 \\ SO_3Na \end{cases} \\ CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases} \end{cases}$	From S acid.
Ponceau 6 R B. Croceine Scarlet 7 B.	$C_6H_3 \begin{cases} N=N-C_6H_3 \begin{cases} CH_3 \\ SO_3Na \end{cases} \\ CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (8)SO_3Na \end{cases} \end{cases}$	From B acid.
Beibrich Scarlet. Ponceau B. Ponceau 3 R B. Fast Ponceau B. New Red L. Imperial Scarlet.	$C_6H_3 \begin{cases} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{cases}$	. .
Ponceau S extra. Fast Ponceau 2 B.	$C_6H_3 \begin{cases} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \quad\quad (2)OH \\ N=N-(1)C_{10}H_4 \begin{cases} (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From R acid.
Orseilline B B.	$C_6H_3 \begin{cases} N=N-C_6H_3 \begin{cases} CH_3 \\ SO_3Na \end{cases} \\ CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.
Manchester Brown E E.	$C_6H_3 \begin{cases} (3)N=N-(1)C_6H_2 \begin{cases} (2)NH_2.HCl \\ (4)NH_2 \\ (5)CH_3 \end{cases} \\ (4)CH_3 \\ (1)N=N-(1)C_6H_2 \begin{cases} (2)NH_2.HCl \\ (4)NH_2 \\ (5)CH_3 \end{cases} \end{cases}$	. .
Naphthylene Red.	$C_{10}H_6 \begin{cases} (1)N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ (5)N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic acid.
Diamine Gold.	$C_{10}H_4 \begin{cases} (1)N=N-(1)C_6H_4(4)OC_2H_5 \\ (3)SO_3Na \\ (7)SO_3Na \\ (5)N=N-(1)C_6H_4(4)OC_2H_5 \end{cases}$	. .
Wool Black.	$C_6H_3 \begin{cases} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \\ N=N-(1)C_{10}H_6(2)C_7H_7NH \end{cases}$	. .

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; red solution.	Violet.	Brown ppt.	Blue.	Red.	Acid dye for wool. Alum dye for cotton.
Brown crystals; red solution.	Brown ppt.	Yellow.	Green.	Red.	Acid dye for wool.
Brown powder; violet solution.	Brown ppt.	Red ppt.	Blue.	Brown ppt.	Acid dye for wool.
Brown powder; red solution.	Browner.	Brown ppt.	Green.	Red ppt.	Acid dye for wool. Soluble in alcohol.
Brown powder; red solution.	Violet.	Red ppt.	Blue.	Red ppt.	Acid dye for wool. Soluble in alcohol.
Brown powder; red solution.	Violet ppt.	Red ppt.	Blue.	Violet.	Acid dye for wool.
Brown powder; orange solution.	Red ppt.	Red ppt.	Green.	Red ppt.	Acid dye for wool.
Brown powder; red solution.	Violet ppt.	No change.	Blue.	Orange.	Acid dye for wool.
Brown powder; red solution.	Yellower.	Violet.	Blue.	Red.	Acid dye for wool.
Brown powder; brown solution.	Brown ppt.	Brown.	Brown.	Brown.	Soluble in alcohol.
Red powder; red solution.	No change.	Black ppt.	Blue.	Black ppt.	Direct dye for cotton.
Orange powder; yellow solution in hot water.	Yellow ppt.	Yellow ppt. Black with excess.	Violet.	Green.	Direct dye for cotton. Soluble in alcohol.
Black powder; violet solution.	Violet ppt.	Violet ppt.	Blue.	Brown ppt.	Acid dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Fast Violet R.	$C_{10}H_6 \begin{cases} (4)N=N-(1)C_6H_4(4)SO_3Na \\ (1)N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases} \end{cases}$	From S acid.
Jet Black R.	$C_{10}H_6 \begin{cases} (4)N=N-C_6H_3(SO_3Na)_2 \\ (1)N=N-(1)C_{10}H_6(4)NHC_6H_5 \end{cases}$	..
Diamond Black.	$C_{10}H_6 \begin{cases} (4)N=N-C_6H_3 \begin{cases} OH \\ CO_2Na \end{cases} \\ (1)N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.
Azonigrine.	$C_{10}H_6 \begin{cases} (4)N=N-C_6H_2 \begin{cases} OH \\ (SO_3Na)_2 \end{cases} \\ (1)N=N-(1)C_{10}H_6(2)OH \end{cases}$	..
Naphthylamine Black D.	$C_{10}H_6 \begin{cases} (4)N=N-C_{10}H_5(SO_3Na)_2 \\ (1)N=N-(1)C_{10}H_6(4)NH_2 \end{cases}$	..
Naphthol Black 6 B. Brilliant Black B.	$C_{10}H_6 \begin{cases} (4)N=N-C_{10}H_5(SO_3Na)_2 \\ (1)N=N-(1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From R acid.
Anthracite Black B.	$C_{10}H_6 \begin{cases} (4)N=N-C_{10}H_5(SO_3Na)_2 \\ (1)N=N-(1)C_6H_3 \begin{cases} (2)NHC_6H_5 \\ (4)NHC_6H_5 \end{cases} \end{cases}$	..
Azo-Black. Blue Black B.	$C_{10}H_6 \begin{cases} (4)N=N-C_{10}H_6.SO_3Na \\ (1)N=N-(1)C_{10}H_4 \begin{cases} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From R acid.
Violet Black.	$C_6H_4 \begin{cases} (1)N=N-(1)C_{10}H_6(4)NH_2 \\ (4)N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.
Naphthol Blue Black.	$C_{10}H_2 \begin{cases} N=N-C_6H_5 \\ (1)NH_2 \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \\ N=N-(1)C_6H_4(4)NO_2 \end{cases}$	From H acid.
Victoria Black B.	$C_{10}H_6 \begin{cases} (1)N=N-(1)C_6H_4(4)SO_3Na \\ (4)N=N-(4)C_{10}H_4 \begin{cases} (1)OH \\ (8)OH \\ SO_3Na \end{cases} \end{cases}$	..
Fast Violet B.	$C_{10}H_6 \begin{cases} (4)N=N-C_6H_3 \begin{cases} CH_3 \\ SO_3Na \end{cases} \\ (1)N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases} \end{cases}$	..
Clayton Wool Brown.	$C_6H \begin{cases} (1)NH_2 \\ (2)NH_2 \\ N=N-C_6H_5 \\ N=N-C_6H_4SO_3Na \\ N=N-C_{10}H_6SO_3Na \end{cases}$	..
Cloth Red 3 B extra.	$C_6H_4 \begin{cases} (2)CH_3 \\ (1)N=N(1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)N=N-(1)C_{10}H_5 \begin{cases} (2)NH.C_2H_5 \\ (7)SO_3Na \end{cases} \end{cases} \end{cases}$	From delta-acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Green powder; violet solution.	Brown ppt.	Violet ppt.	Blue.	Violet ppt.	Acid dye for wool. Soluble in alcohol.
Black powder; violet solution.	Violet ppt.	Black ppt.	Blue.	Blue ppt.	Acid dye for wool. Soluble in alcohol.
Black powder; violet solution.	Blue.	Violet ppt.	Green.	Violet ppt.	Soluble in alcohol. Dyes chromed wool.
Black powder; black solution.	No change.	Red.	Greenish.	Red ppt.	Acid dye for wool.
Black powder; black solution.	No change.	Black ppt.	Bluish.	Black ppt.	Acid dye for wool.
Black powder; violet solution.	Blue.	No change.	Greenish.	Violet ppt.	Acid dye for wool.
Black powder; violet solution.	No change.	Violet ppt.	Black.	Greenish.	Acid dye for wool.
Black powder; violet solution.	Blue ppt.	Blue ppt.	Green.	Blue ppt.	Acid dye for wool.
Bronze powder; red solution.	Violet.	Violet ppt.	Blue.	Violet ppt.	Direct dye for cotton. Precipitated by magenta.
Black powder; blue solution.	No change.	Blue ppt.	Green.	Blue ppt.	Soluble in alcohol.
Black powder; violet solution.	Bluer.	Redder.	Blue.	Reddish.	Acid dye for wool.
Brown powder; violet solution.	Violet ppt.	Violet ppt.	Green.	Violet ppt.	Soluble in alcohol. Acid dye for wool.
Brown powder; brown solution.	No change.	No change.	. .	. .	. .
Brown powder; red solution.	Brown ppt.	Brown ppt.	Green.	Red.	Soluble in alcohol. Acid dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Fast Azo-Granat. Fat Ponceau.	$C_6H_4 \begin{cases} (2)CH_3 \\ (1)N{=}N(1)C_6H_3 \end{cases} \begin{cases} (3)CH_3 \\ (4)N{=}N{-}(1)C_{10}H_6(2)OH \end{cases}$	Developed on fibre.
Milling Orange.	$C_6H_4 \begin{cases} (2)SO_3Na \\ (5)N{=}N{-}(3)C_6H_3(6)N{=}N{-}(2)C_6H_3 \end{cases} \begin{cases} (4)CO_2H \\ (5)OH \end{cases}$	From salicylic acid.
Leather Brown.	$C_6H_4 \begin{cases} (1)NHC_2H_3O \\ (4)N{=}N(1)C_6H_2 \end{cases} \begin{cases} (2)NH_2 \\ (4)NH_2 \\ (5)N{=}N{-}(1)C_6H_4(4)NHC_2H_3O \end{cases}$	. .
Cotton Orange R.	$C_6H_4 \begin{cases} (1)SO_3Na \\ (3)N{=}N{-}(1)C_6 \end{cases} \begin{cases} (2)NH_2 \\ (4)SO_3Na \\ (5)SO_3Na \\ (6)NH_2 \\ (3)N{=}N{-}P \end{cases}$ (P = Primuline base.)	From primuline and metanilic acid.
Heligoland Yellow.	$C_6H_4 \begin{cases} (1)OH \\ (4)N{=}N(1)C_6H_4(4)NH.CS.NH.C_6H_4.N{=}N.C_6H_4OH \end{cases}$	. .

Azo-Dyes from Benzidine and its Analogues.[1]

During the last few years a group of new coal-tar dyes have been introduced,[2] which possess the characteristic property of dyeing cotton in a neutral or alkaline bath without a mordant, a peculiarity previously confined to a few natural coloring matters (e. g., turmeric, safflower, annatto). The new dyes belong to the class of tetrazo- or secondary azo-compounds, but differ from those previously described (page 178 et seq.) by containing two benzene nuclei in the azo-group, being derived from diazo-diphenyl (diazotized benzidine) or its analogues. They all contain a sulpho- or carboxyl group, and occur in commerce as sodium salts.

When an alcoholic solution of nitrobenzene is treated with caustic soda and zinc-dust, a z o b e n z e n e, $C_6H_5.N_2.C_6H_5$, is formed. This body is converted by boiling with zinc-dust into h y d r a z o - b e n z e n e, $C_6H_5.NH.NH.C_6H_5$, and this on treatment with strong hydrochloric acid is converted by a molecular change into b e n z i - d i n e, which is precipitated on adding excess of ammonia.

Benzidine has the constitution of a diamido-diphenyl in which

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[1] A very valuable paper on the Benzidine and Allied Colors, from which much of the information in the text is derived, has been published by G. H. Hurst (*Jour. Soc. Dyers*, etc., iv. 14).

[2] Congo Red, discovered by Bœttiger in 1884, was the first of these dyestuffs.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; insoluble.	Violet with alcohol solution.	. .	Green.	Red ppt.	Soluble in alcohol. Ingrain color.
Brown powder; orange solution.	Red ppt.	Yellow ppt.	Violet.	Yellow ppt.	Chrome dye for wool.
Black powder; brown solution.	Brown ppt.	Darker.	Brown.	. .	Dye for leather.
Brown powder; orange solution.	No change.	Red ppt.	Red.	Red ppt.	Direct dye for cotton.
Brown powder; yellow solution.	Redder.	Brown ppt.	Orange.	Brown ppt.	Direct dye for cotton.

both the NH_2 groups occupy the para-position. When the di-hydrochloride is treated in acid solution with nitrous acid or sodium nitrite it is diazotized, forming t e t r a z o - d i p h e n y l dichloride, according to the following equation:—

$$\begin{matrix} C_6H_4.NH_2.HCl \\ | \\ C_6H_4.NH_2.HCl \end{matrix} + 2HNO_2 = 4H_2O + \begin{matrix} C_6H_4.N:N.Cl \\ | \\ C_6H_4.N:N.Cl \end{matrix}$$
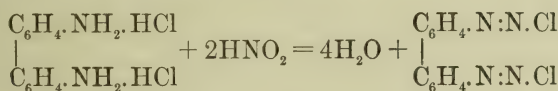
By reaction with aromatic amines or phenols, or their derivatives, the tetrazo-diphenyl dichloride forms the series of coloring matters known as the b e n z i d i n e d y e s, of which *congo-red* is the type. To produce this substance, the solution of one molecule of tetrazo-diphenyl dichloride is added to a well-cooled solution of two molecules of sodium naphthionate, and then sodium acetate added:—

$$\begin{matrix} C_6H_4.N_2.Cl \\ | \\ C_6H_4.N_2.Cl \end{matrix} + 2C_{10}H_6(SO_3Na)NH_2$$

$$= 2HCl + \begin{matrix} C_6H_4.N_2.C_{10}H_5(SO_3Na).NH_2 \\ | \\ C_6H_4.N_2.C_{10}H_5(SO_3Na).NH_2. \end{matrix}$$
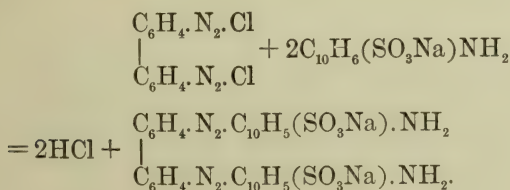
The reaction requires several hours for its completion, and occurs in two distinct stages, an intermediate product being first obtained. This is of general occurrence under similar circumstances, and by taking advantage of the fact it is possible to combine one molecule of diazotized benzidine or an analogous body with two different phenols, amines, etc. Thus *congo corinth* is obtained by first reacting on one molecule of tetrazo-diphenyl dichloride with one molecule of sodium alphanaphthylamine-sulphonate, and treating the intermediate product thus obtained with sodium alphanaphthol-sulphonate:—

$$
\begin{aligned}
&\begin{array}{l}
C_6H_4 - N = N - (2)C_{10}H_5 \left\{ \begin{array}{l} (1)NH_2 \\ (4)SO_3Na \end{array} \right. + C_{10}H_6 \left\{ \begin{array}{l} (1)OH \\ (4)SO_3Na \end{array} \right. \\
C_6H_4 - N = N - Cl
\end{array} \\[2ex]
&= HCl + \begin{array}{l}
C_6H_4 - N = N - (2)C_{10}H_5 \left\{ \begin{array}{l} (1)NH_2 \\ (4)SO_3Na \end{array} \right. \\
C_6H_4 - N = N - (2)C_{10}H_5 \left\{ \begin{array}{l} (1)NH_2 \\ (4)SO_3Na. \end{array} \right.
\end{array}
\end{aligned}
$$
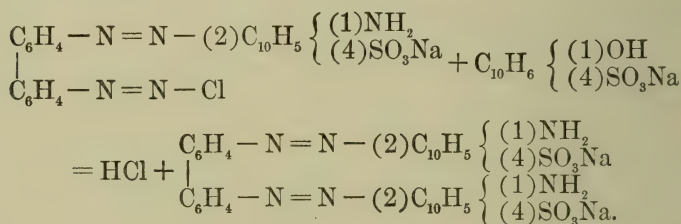
By processses similar to those employed for the preparation of benzidine, the homologous base, t o l i d i n e, $(NH_2).C_6H_3(CH_3).$ $C_6H_3(CH_3).(NH_2)$, can be prepared from n i t r o t o l u e n e, $C_6H_4(CH_3)(NO_2)$; and when diazotized, tolidine yields t e t r a z o-d i t o l y l d i c h l o r i d e, homologous with the similar product from benzidine. This body reacts with phenols, aromatic amines, etc., in the same way as its lower homologue. *Benzopurpurin* and *azo-blue* are examples of coloring matters thus obtained.

By first sulphonating paranitrotoluene, and treating the product with zinc-dust and caustic soda, it is converted into d i a m i d o-s t i l b e n e - d i s u l p h o n i c a c i d, and this when diazotized in hydrochloric acid solution yields the dichloride of t e t r a z o-s t i l b e n e - d i s u l p h o n i c a c i d:—

$$
\begin{aligned}
&\begin{array}{l}
CH.C_6H_3(SO_3H).NH_2 \\
CH.C_6H_3(SO_3H).NH_2
\end{array} + 2HNO_2 \\[2ex]
&= 4H_2O + \begin{array}{l}
CH.C_6H_3(SO_3H).N_2.Cl \\
CH.C_6H_3(SO_3H).N_2.Cl.
\end{array}
\end{aligned}
$$
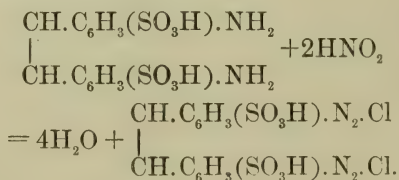
This body can react with phenols, amines, etc., to form coloring matters, of which *brilliant yellow* and the *Hessian purples* are examples.

Similar coloring matters are obtainable from d i a m i d o - f l u o -
r e n e, $C_{13}H_8(NH_2)_2$.

As already stated, all the coloring matters of the class under
consideration dye cotton in a neutral or slightly alkaline bath,
without the aid of a mordant.   In practice, the cotton is boiled in
a solution of dye rendered alkaline by soap and sodium phosphate
and carbonate.   Borate, silicate, and stannate of sodium are also
used.

The benzidine dyes can also be used for wool, but an alkaline
bath is an objection.   With some of them a bath acidulated with
acetic acid can be employed.   The colors produced on wool by the
blue and violet dyes of this class are always much redder in shade
than are given by the same dyes on cotton.   The colors on wool
are faster to light than those on cotton, and may be rendered fast
to milling by the addition of acetic acid or ammonium acetate to
the dye-bath, or in some cases, by an after treatment with bichro-
mate of potash.   An after treatment with copper sulphate solution
also renders many of the benzidine colors faster to light on wool.

The fastness against light and fulling of a number of the benzi-
dine colors may be very materially increased when dyed on cotton
by a subsequent treatment with such metallic salts as copper
sulphate, chromium fluoride, and potassium bichromate.   In
some cases the shade is not much altered by this process, whilst in
others the shade is changed considerably, generally being rendered
duller.   Copper sulphate appears to have more influence on the
shade than the chromium salts.   The exact chemical effect of
these metallic salts on the dyestuff is not known with any cer-
tainty.   It has been supposed that treatment with copper sulphate
causes a film of a copper compound to be precipitated on the fibre
which serves to protect the color underneath from the action of
light.   Potassium bichromate no doubt exerts an oxidizing
influence.

COMMERCIAL NAME.	FORMULA.	REMARKS.
From Benzidine. Chrysamine G. Flavophenin.	C_6H_4—N=N—(4)$C_6H_3 \begin{cases} (1)OH \\ (2)CO_2H \end{cases}$ C_6H_4—N=N—(4)$C_6H_3 \begin{cases} (1)OH \\ (2)CO_2H \end{cases}$	From salicylic acid.
Congo yellow.	C_6H_4—N=N—NH(4)C_6H_4(1)SO_3Na C_6H_4—N=N—(4)C_6H_4(1)OH	From sulphanilic acid and phenol.
Congo Red.	C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$ C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From naphthionic acid.
Deltapurpurin G.	C_6H_4—N=N—(1)$C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases}$ C_6H_4—N=N—(1)$C_{10}H_5 \begin{cases} (7)NH_2 \\ (2)SO_3Na \end{cases}$	From β-naphthylamine sulphonic acid.
Brilliant Congo G.	C_6H_4—N=N—(1)$C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases}$ C_6H_4—N=N—(1)$C_{10}H_4 \begin{cases} (6)SO_3Na \\ (3)SO_3Na \\ (2)NH_2 \end{cases}$	From R acid.
Sulphanil yellow. Parasulphurine S.	C_6H_4—N=N—NH(4)C_6H_4(1)SO_3Na C_6H_4—N=N—NH(4)C_6H_4(1)SO_3Na	From sulphanilic acid.
Azo-orseilline.	C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases}$ C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases}$	From N W acid.
Bordeaux Extra. Congo Violet. Bordeaux C O V.	C_6H_4—N=N—(1)$C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases}$ C_6H_4—N=N—(1)$C_{10}H_5 \begin{cases} (2)OH \\ (6)SO_3Na \end{cases}$	From β acid.
Congo Corinth G.	C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$ C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From N W acid.
Congo G.	C_6H_4—N=N—NH(1)C_6H_4(3)SO_3Na C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From sulphanilic and naphthionic acid.
Alkali Red.	C_6H_4—N=N—$C_{10}H_4 \begin{cases} NH_2(a) \\ (SO_3Na)_2 \end{cases}$ C_6H_4—N=N—(2)$C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From naphthylamine disulphonic and naphthionic acids.
Congo P.	C_6H_4—N=N—(1)$C_{10}H_4 \begin{cases} (2)OH \\ (6)SO_3Na \\ (8)SO_3Na \end{cases}$ C_6H_4—N=N—(1)C_6H_4(4)OH	From G (γ) acid.
Direct Red B. Diamine Scarlet B.	C_6H_4—N=N—(1)C_6H_4(4)OC_2H_5 C_6H_4—N=N—(1)$C_{10}H_4 \begin{cases} (2)OH \\ (6)SO_3Na \\ (8)SO_3Na \end{cases}$	From G acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; yellow solution.	Brown.	Brown ppt.	Violet.	Brown ppt.	Brown ppt. with acetic acid.
Yellow paste; yellow solution.	Brown.	Brown ppt.	Red.	Brown ppt.	Brown ppt. with acetic acid.
Brown powder; brown solution.	Brown ppt.	Blue ppt.	Blue.	Blue ppt.	Violet ppt. with acetic acid.
Red powder; orange solution in hot water.	No change.	Brown ppt.	Blue.	Brown ppt.	Red ppt. with acetic acid. Obsolete. Precipitated by magenta.
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Precipitated by magenta.
Yellow paste; yellow solution.	No change.	. .	Decomposed, nitrogen evolved on heating.	. .	. .
Violet paste; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	. .
Brown powder; red solution.	Yellower.	Violet ppt.	Violet.	Violet ppt.	. .
Black powder; red solution.	Redder.	Violet ppt.	Blue.	Violet ppt.	Violet solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Violet ppt. with acetic acid.
Red powder; red solution.	No change.	Blue ppt.	Blue.	Violet ppt.	Slightly soluble in alcohol. Obsolete.
Red powder; red solution.	Brown.	Brown ppt.	Violet.	Brown.	Soluble in alcohol.
Red crystals; red solution.	No change.	Brown.	Violet.	Brown.	Soluble in alcohol. Acid dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Alkali Yellow R.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-NH(4).C_6H_3 \begin{cases} (2)SO_3Na \\ (1)C{<}^{N(1)}_{S(2)} \end{cases} C_6H_3(4)CH_3.$	From salicylic acid.
Cloth Orange.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2H \end{cases}$ $C_6H_4-N=N-(4)C_6H_3 \begin{cases} (1)OH \\ (3)OH \end{cases}$	From salicylic acid.
Benzo Orange R.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From salicylic acid.
Cloth Brown G.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2H \end{cases}$ $C_6H_4-N=N-(1)C_{10}H_5 \begin{cases} (2)OH \\ (7)OH \end{cases}$	From salicylic acid.
Cloth Brown R.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-C_{10}H_5 \begin{cases} SO_3Na \\ OH \end{cases}$	From salicylic acid.
Brahma Red, B and B B.	$C_6H_4-N=N-(4)C_6H_4(1)NH.C_6H_4.SO_3Na$ $C_6H_4-N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From naphthionic acid.
Brahma Orange.	$C_6H_4-N=N-(4)C_6H_4(1)NH.C_6H_4.SO_3Na$ $C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$	From salicylic acid.
Brahma Red 6 B.	$C_6H_4-N=N-C_6H_4.NH.C_{10}H_6.SO_3Na$ $C_6H_4-N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From naphthionic acid.
Naphtho-cyanin.	$C_6H_4-N=N-C_{10}H_4 \begin{cases} (1)OH \\ (5)OH \\ SO_3Na \end{cases}$ $C_6H_4-N=N-C_{10}H_4 \begin{cases} (1)OH \\ (5)OH \\ SO_3Na \end{cases}$	From dioxy-naph-thalene.
Carbazol Yel-low.	$C_6H_3\underset{\diagdown NH}{-N=N-C_6H_3} \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_3-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$	From salicylic acid.
Congo Brown R.	$C_6H_4-N=N-(4)C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-(4)C_6H_2 \begin{cases} (1)OH \\ (3)OH \\ (2)N=N-(1)C_{10}H_6(4)SO_3Na \end{cases}$	From Cloth Orange with naphthionic acid.
Congo Brown G.	$C_6H_4-N=N-(4)C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-(4)C_6H_2 \begin{cases} (1)OH \\ (3)OH \\ (2)N=N-(1)C_6H_4(4)SO_3Na \end{cases}$	From Cloth Orange with sulphanilic acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Yellow powder; yellow solution.	Orange ppt.	Yellow ppt.	Red.	Yellow ppt.	. . .
Brown powder; brown solution.	Red ppt.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol. Dyes chromed wool.
Red crystals; orange solution.	Orange ppt.	Violet.	Violet.	Violet ppt.	. . .
Brown powder; brown solution.	Brown-red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol. Dyes chromed wool.
Red powder; brown solution.	Red ppt.	Brown ppt.	Violet.	Brown ppt.	Dyes chromed wool.
Brown powder; red solution.	No change.	Black ppt.	Blue.	Violet ppt.	Soluble in alcohol. Obsolete.
Brown powder; brown solution.	. .	Black ppt.	Red.	Black ppt.	Obsolete.
Brown powder; red solution.	Brighter.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol. Obsolete.
Brown powder; red solution.	Brighter.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol. Obsolete.
Yellow powder; yellow solution.	Orange.	Brown ppt.	Blue.	Brown ppt.	. . .
Red powder; red solution.	Red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; red solution.	Red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Hessian Brown B B.	$C_6H_4-N=N-(2)C_6H_2 \begin{cases} (1)OH \\ (3)OH \\ (4)N=N-(1)C_6H_4(4)SO_3Na \end{cases}$ $C_6H_4-N=N-(2)C_6H_2 \begin{cases} (1)OH \\ (3)OH \\ (4)N=N-(1)C_6H_4(4)SO_3Na \end{cases}$	From Resorcin yellow.
Benzo Gray.	$C_6H_4-N=N-(2)C_6H_3 \begin{cases} (1)OH \\ (4)CO_2Na \end{cases}$ $C_6H_4-N=N-(4)C_{10}H_6(1)-N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases}$	From N W acid.
Direct Gray R.	$C_6H_4-N=N-C_{10}H_3 \begin{cases} (OH)_2 \\ CO_2Na \\ SO_3Na \end{cases}$ $C_6H_4-N=N-C_{10}H_3 \begin{cases} (OH)_2 \\ CO_2Na \\ SO_3Na \end{cases}$	From β-oxynaph-thoic acid.
Diamine Black R.	$C_6H_4-N=N-C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$ $C_6H_4-N=N-C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$	From G acid.
Diamine Fast Red.	$C_6H_4-N=N-(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$ $C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$	From G acid.
Diamine Brown V.	$C_6H_4-N=N-C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$ $C_6H_4-N=N-(4)C_6H_3 \begin{cases} (1)NH_2 \\ (3)NH_2 \end{cases}$	From G acid.
Diamine Violet N.	$C_6H_4-N=N-(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$ $C_6H_4-N=N-(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (8)OH \\ (6)SO_3Na \end{cases}$	From G acid.
Diamine Blue B B.	$C_6H_4-N=N-C_{10}H_3 \begin{cases} (1)NH_2 \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases}$ $C_6H_4-N=N-C_{10}H_3 \begin{cases} (1)NH_2 \\ (8)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{cases}$	From H acid.
Diamine Bronze G.	$C_6H_4-N=N-C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases}$ $C_6H_4-N=N-C_{10}H_3 \begin{cases} (1)OH \\ (3)SO_3Na \\ (6)SO_3Na \\ (8)N=N(4)C_6H_3 \begin{cases} (3)NH_2 \\ (1)NH_2 \end{cases} \end{cases}$	From H acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; brown solution.	Red.	Brown ppt.	Black.	Brown ppt.	Soluble in alcohol.
Gray powder; brown solution.	No change.	Black ppt.	Blue.	Black ppt.	. . .
Gray powder; violet solution.	Violet red.	Gray ppt.	Blue.	Gray ppt.	. . .
Black powder; violet solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.
Red powder; red solution.	No change.	Brown ppt.	Blue.	Brown ppt.	Soluble in alcohol.
Black powder; red solution in hot water.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; violet solution.	No change.	Black ppt.	Blue.	Violet ppt.	. . .
Gray powder; violet solution.	No change.	No change.	Blue.	Violet.	. . .
Black powder; brown solution in hot water.	Yellower.	Purple ppt.	Violet.	Black ppt.	. . .

COMMERCIAL NAME.	FORMULA.	REMARKS.
Diamine Green B.	$C_6H_4-N=N-(4)C_6H_4(1)OH$ $\quad\mid\qquad\qquad\begin{cases}(1)OH\\(2)NH_2\end{cases}$ $C_6H_4-N=N-C_{10}H_2\begin{cases}(3)SO_3Na\\(6)SO_3Na\\N=N-(1)C_6H_4(4)NO_2\end{cases}$	. . .
Sulphone Azurin.	$SO_2\begin{cases}C_6H_2\begin{cases}SO_3Na\\N=N-(1)C_{10}H_6(2)NHC_6H_5\end{cases}\\C_6H_2\begin{cases}N=N-(1)C_{10}H_6(2)NHC_6H_5\\SO_3Na\end{cases}\end{cases}$	From benzidine sulphone.
Cotton Bordeaux.	$C_6H_3\begin{cases}N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\\(2)>C=N-OH\\ \end{cases}$ $C_6H_3\begin{cases}(2)\\N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\end{cases}$	From diamido-diphenylene - ketoxime with naphthionic acid.
Diamine Red N O.	$C_6H_3\begin{cases}(3)OC_2H_5\\N=N-(1)C_{10}H_5\begin{cases}(2)NH_2\\(6)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(1)C_{10}H_5\begin{cases}(7)SO_3Na\\(2)NH_2\end{cases}$	From ethoxybenzidine.
Diamine Blue B.	$C_6H_3\begin{cases}(3)OC_2H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(7)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(2)C_{10}H_5\begin{cases}(4)SO_3Na\\(1)OH\end{cases}$	From ethoxybenzidine.
Diamine Blue 3 R.	$C_6H_3\begin{cases}(3)OC_2H_5\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}$	From ethoxybenzidine and N W acid.
Diamine Black B.	$C_6H_3\begin{cases}(3)OC_2H_5\\N=N-(5)C_{10}H_4\begin{cases}(2)NH_2\\(8)OH\\(6)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(5)C_{10}H_4\begin{cases}(2)NH_2\\(8)OH\\(6)SO_3Na\end{cases}$	From ethoxybenzidine and G acid.
Diamine Blue Black E.	$C_6H_3\begin{cases}(3)OC_2H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(7)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(5)C_{10}H_4\begin{cases}(2)NH_2\\(8)OH\\(6)SO_3Na\end{cases}$	From ethoxybenzidine and G acid.
Benzo-Azurin G.	$C_6H_3\begin{cases}(3)OCH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$ $C_6H_3\begin{cases}(3)OCH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From dianisidine and N W acid.
Azo-Violet.	$C_6H_3\begin{cases}(3)OCH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\end{cases}$ $C_6H_3\begin{cases}(3)OCH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\end{cases}$	From dianisidine and N W acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Black powder; green solution.	Yellower.	Black ppt.	Violet.	Black ppt.	Soluble in alcohol.
Dark blue powder; blue solution.	Blue ppt.	Blue ppt.	Violet.	Violet ppt.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	Blue ppt.	Blue.	Blue ppt.	. . .
Green crystals; red solution.	No change.	Violet ppt.	Blue.	Black ppt.	Soluble in alcohol.
Bronze powder; blue solution.	Violet.	Blue ppt.	Blue.	Blue ppt.	. . .
Black powder, violet solution.	Redder.	No change.	Blue.	Violet ppt.	Soluble in alcohol.
Black powder; blue solution.	No change.	Blue ppt.	Blue.	Violet ppt.	Soluble in alcohol. Yields ingrain colors.
Black powder; blue solution.	No change.	Blue ppt.	Blue.	Blue ppt.	. . .
Black powder; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	Dyed color becomes red on heating and blue again on cooling. Precipitated by magenta.
Blue powder; violet solution.	Red.	Blue ppt.	Blue.	Blue ppt.	Violet color with acetic acid. Precipitated by magenta.

Commercial Name.	Formula.	Remarks.
Heliotrope.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(1)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(1)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.$	From dianisidine and δ acid.
Benzo-azurin 3 G.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)OH\\(5)SO_3Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)OH\\(5)SO_3Na\end{array}\right.$	From dianisidine and L acid.
Benzo-pur-purin 10 B.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.$	From dianisidine and naphthionic acid.
Brilliant Azurin 5 G.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-C_{10}H_4\end{array}\right.\left\{\begin{array}{l}(1)OH\\(8)OH\\(4)SO_3Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-C_{10}H_4\end{array}\right.\left\{\begin{array}{l}(1)OH\\(8)OH\\(4)SO_3Na\end{array}\right.$	From dianisidine.
Diamine Sky Blue.	$C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\N=N-C_{10}H_3\end{array}\right.\left\{\begin{array}{l}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\N=N-C_{10}H_3\end{array}\right.\left\{\begin{array}{l}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.$	From diphenetidine and H acid.
Benzo Black Blue G.	$C_6H_3\left\{\begin{array}{l}SO_3Na\\N=N-(4)C_{10}H_6(1)N=N(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)OH\\(4)SO_2Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}SO_3Na\\N=N-(2)C_{10}H_5\end{array}\right.\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.$	From N W acid.
New Red.	$C_6H_3\left\{\begin{array}{l}(2)NO_2\\N=N-(4)C_6H_3\end{array}\right.\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.$	From nitrobenzi-dine.
Direct Blue B.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-C_{10}H_3\end{array}\right.\left\{\begin{array}{l}(OH)_2\\SO_3Na\\CO_2Na\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\N=N-C_{10}H_5\end{array}\right.\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right.$	From dianisidine.
Benzo Indigo Blue.	$C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\N=N-(4)C_{10}H_6(1)NH_2\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\N=N-(4)C_{10}H_4\end{array}\right.\left\{\begin{array}{l}SO_3Na\\(1)OH\\(8)OH\end{array}\right.$	From ethoxyben-zidine.
Glycin Corinth.	$C_6H_4-N=N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $C_6H_4-N=N-(1)C_{10}H_6(4)NH.CH_2.CO_3Na$	. . .

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARAC- TERISTICS.
	With Caustic Soda.	With Hy- drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Violet color with acetic acid.
Black powder; violet solu- tion.	Violet red.	Violet ppt.	Blue.	Violet ppt.	Soluble in alco- hol.
Red powder; red solution.	Red ppt.	Blue ppt.	Blue.	Blue ppt.	Soluble in alco- hol.
Black powder; violet solu- tion.	Red.	Blue ppt.	Greenish- blue.	Violet ppt.	Soluble in alco- hol.
Gray powder; blue solution.	Redder.	No change.	Green.	Blue.	. . .
Black powder; blue black solution.	Blue.	Blue ppt.	Green.	Blue ppt.	. . .
Red powder; red solution in hot water.	No change.	Red ppt.	Red.	Orange.	Acid or chrome dye for wool.
Black powder; blue solution.	Violet.	Black ppt.	Blue.	Violet ppt.	Soluble in alco- hol.
Gray powder; blue solution.	Violet ppt.	Blue ppt.	Blue.	Blue ppt.	. . .
Brown powder; violet solu- tion.	Red ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alco- hol. Direct dye for cot- ton.

Commercial Name.	Formula.	Remarks.
Glycin Red.	$C_6H_4-N=N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $\overset{\mid}{C}_6H_4-N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}$	. . .
Glycin Blue.	$C_6H_3-N=N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $\overset{\mid}{\underset{\mid}{>}}SO_2$ $C_6H_3-N=N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$	. . .
Heliotrope 2 B.	$C_6H_4-N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(8)SO_3Na\end{cases}$ $\overset{\mid}{C}_6H_4-N=N-(2)C_{10}H_4\begin{cases}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{cases}$	From Sch. acid.
Rouge M.	$C_6H_4-N=N-(1)C_{10}H_5\begin{cases}(2)NH_2\\(4)OH\end{cases}$ $\overset{\mid}{C}_6H_4-N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}$	. . .
Oxamine Violet.	$C_6H_4-N=N-(2)C_{10}H_4\begin{cases}(1)OH\\(3)SO_3Na\\(6)NH_2\end{cases}$ $\overset{\mid}{C}_6H_4-N=N-(2)C_{10}H_4\begin{cases}(1)OH\\(3)SO_3Na\\(6)NH_2\end{cases}$	. . .
Anthracene Red.	$C_6H_3\begin{cases}(3)NO_2\\N=N-(1)C_6H_3\begin{cases}(3)CO_2Na\\(4)OH\end{cases}\end{cases}$ $\overset{\mid}{C}_6H_4-N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}$	From salicylic and N W acids.
Dianisidine Blue.	$C_6H_3\begin{cases}(3)O.CH_3\\N=N-(1)C_{10}H_6(2)OH\end{cases}$ $\overset{\mid}{C}_6H_3\begin{cases}(3)O.CH_3\\N=N-(1)C_{10}H_6(2)OH\end{cases}$	Developed on the fibre.
Diamine Pure Blue. Benzo and Congo Pure Blues.	$C_6H_3\begin{cases}(3)O.CH_3\\N=N-(2)C_{10}H_3\begin{cases}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{cases}\end{cases}$ $\overset{\mid}{C}_6H_3\begin{cases}(3)O.CH_3\\N=N-(2)C_{10}H_3\begin{cases}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{cases}\end{cases}$	From H acid.
Toluylene Brown G.	$N-(2)C_6H_2\begin{cases}(1)CH_3\\(5)SO_3Na\\(4)N\end{cases}$ $N-(2)C_6H_2\begin{cases}(4)N\\(5)NH_2\\(1)NH_2\end{cases}$	. . .
Toluylene Orange R R.	$C_6H_2\begin{cases}(2)N=N-(1)C_{10}H_6(2)NH_2\\(3)SO_3Na\\(5)CH_3\\(6)N=N-(1)C_{10}H_6(2)NH_2\end{cases}$	. . .

CHARACTER OF OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; orange solution.	Orange ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Dark powder; red solution.	Red ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Gray powder; violet solution.	Redder.	Violet ppt.	Blue.	Violet.	Soluble in alcohol. Direct dye for cotton.
Red powder; red solution.	Orange.	Brown ppt.	Blue.	Colorless.	Direct dye for cotton.
Green powder; violet solution.	Violet ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Brown powder; red solution.	No change.	Red ppt.	Red.	Brown ppt.	Soluble in alcohol. Acid and chrome dye for wool.
. . .	. .	. .	. .	. .	Ingrain color.
Black powder; blue solution.	Redder.	No change.	Green.	Blue.	Direct dye for cotton.
Brown powder; brown solution.	No change.	Brown ppt.	Red.	. .	Direct dye for cotton.
Red powder; orange solution.	Orange ppt.	Brown ppt.	Blue.	. .	Soluble in alcohol. Direct dye for cotton.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Pyramine Orange.	$C_6H_3\begin{cases}(2)SO_3Na\\N=N-(1)C_6H_2\begin{cases}(2)NH_2\\(4)NH_2\\(5)NO_2\end{cases}\end{cases}$ $C_6H_3\begin{cases}(2)SO_3Na\\N=N-(1)C_6H_2\begin{cases}(2)NH_2\\(4)NH_2\\(5)NO_2\end{cases}\end{cases}$	. . .
Diamin Catechin.	$C_{10}H_4\begin{cases}(1)N=N-(1)C_{10}H_6(4)OH\\(3)SO_3H\\(7)SO_3H\\(5)N=N-(1)C_{10}H_6(4)OH\end{cases}$	From diazotized naphth y l e n e violet; developed on the fibre.
Naphthyl Blue 2 B.	$C_6H_3\begin{cases}(3)CO_2Na\\N=N-C_{10}H_4\begin{cases}(1)NH.CO.C_6H_5\\(8)OH\\(5)SO_3Na\end{cases}\end{cases}$ $C_6H_3\begin{cases}(3)CO_2Na\\N=N-C_{10}H_4\begin{cases}(1)NH.CO.C_6H_5\\(8)OH\\(5)SO_3Na\end{cases}\end{cases}$	From ortho-diamido-diphenic acid.
Benzo Olive.	$C_6H_4-N=N-(1)C_6H_3\begin{cases}(3)CO_2Na\\(4)OH\end{cases}$ $C_6H_4-N=N-(1)C_{10}H_6(4)N=N-C_{10}H_3\begin{cases}OH\\NH_2\\(SO_3Na)_2\end{cases}$	From H acid.
Benzo Black Blue 5 G.	$C_6H_3\begin{cases}(3)SO_3Na\\N=N-C_{10}H_4\end{cases}\begin{cases}(OH)_2\\SO_3Na\end{cases}$ $C_6H_3\begin{cases}(3)SO_3Na\\N=N-C_{10}H_6(4)N=N-C_{10}H_4\end{cases}\begin{cases}(OH)_2\\SO_3Na\end{cases}$	From S acid.
Alizarin Yellow F S.	$M\begin{cases}N=N-C_6H_3\begin{cases}OH\\CO_2Na\end{cases}\\N=N-C_6H_3\begin{cases}OH\\CO_2Na\end{cases}\\N=N-C_6H_3\begin{cases}OH\\CO_2Na\end{cases}\end{cases}$ (M = magenta base.)	From magenta and salicylic acid.
Mekong Yellow G.	$C_6H_4-N=N-C_6H_3\begin{cases}OH\\CO_2Na\end{cases}$ $\begin{matrix}C_6H_4-N=N-C_6H_3OH\\C_6H_4-N=N-C_6H_3OH\end{matrix}\Big\}CH_2$ $C_6H_4-N=N-C_6H_3\begin{cases}OH\\CO_2Na\end{cases}$	From salicylic acid.
From Diamido-phenyl-tolyl. Direct Yellow.	$C_6H_3\begin{cases}(3)CH_3\\N=N-C_6H_3\begin{cases}(1)OH\\(2)CO_2Na\end{cases}\end{cases}$ $C_6H_4-N=N-C_6H_3\begin{cases}(1)OH\\(2)CO_2Na\end{cases}$	From salicylic acid.
Direct Red.	$C_6H_3\begin{cases}(3)CH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\end{cases}$ $C_6H_4-N=N-(2)C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}$	From naphthionic acid.
Diamine Yellow W.	$C_6H_3\begin{cases}(3)CH_3\\N=N-C_6H_3\begin{cases}(1)OH\\(4)CO_2H\end{cases}\end{cases}$ $C_6H_4-N=N-(4)C_6H_4(1)OC_2H_5$	From salicylic acid.

	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		
CHARACTER OF DYESTUFF.	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	OTHER CHARACTERISTICS.
Red powder; orange solution.	Orange ppt.	Orange ppt.	Yellow.	Orange ppt.	Direct dye for cotton.
. . .	. .	. .	. .	. .	Ingrain color.
Blue powder; blue solution.	Violet.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Black powder; green solution.	Brown.	Green ppt.	Violet.	Black ppt.	Direct dye for cotton.
Gray powder; blue solution.	No change.	Green ppt.	Green.	Green ppt.	Direct dye for cotton.
Brown paste; insoluble in water.	Orange solution.	. .	Green.	. .	Slightly soluble in alcohol. Chrome dye for wool.
Brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.
Brown powder; yellow solution.	Brown.	Brown ppt.	Red.	Brown ppt.	Soluble in alcohol.
Red powder; red solution.	Red ppt.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.
Yellow powder; yellow solution.	Orange ppt.	Green ppt.	Violet.	Brown ppt.	Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Chrysamine R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}C_6H_3 \begin{cases} (1)OH \\ (2)CO_2Na \end{cases} \end{cases}$	From salicylic acid.
Toluylene Orange G.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(4)C_6H_2 \begin{cases} (6)CH_3 \\ (1)OH \\ (2)CO_2Na \\ (5)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(4)C_6H \begin{cases} (1)NH_2 \\ (3)NH_2 \\ (6)CH_3 \end{cases} \end{cases}$	From cresotic acid.
Toluylene Orange R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(4)C_6H \begin{cases} (6)CH_3 \\ (1)NH_2 \\ (3)NH_2 \\ (5)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(4)C_6H \begin{cases} (6)CH_3 \\ (1)NH_2 \\ (3)NH_2 \\ (5)SO_3Na \end{cases} \end{cases}$	. . .
Rosazurin G.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NHC_2H_5 \\ (7)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (7)SO_3Na \end{cases} \end{cases}$	From δ acid.
Rosazurin B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NHC_2H_5 \\ (7)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NHC_2H_5 \\ (7)SO_3Na \end{cases} \end{cases}$	From δ acid.
Diamine Red 3 B. Deltapurpurin 7 B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (7)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (7)SO_3Na \end{cases} \end{cases}$	From δ acid.
Brilliant Purpurin.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic and R acids.
Congo Orange R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}(1)C_6H_4(4)OC_2H_5 \end{cases}$	From R acid and phenol.
Azo Mauve.	$C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}C_{10}H_3 \begin{cases} NH_2 \\ OH \\ (SO_3Na)_2 \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N{=}N{-}C_{10}H_6.NH_2 \end{cases}$	. . .

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARAC- TERISTICS.
	With Caustic Soda.	With Hy- drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; yellow solu- tion.	Brown.	Brown ppt.	Violet.	Brown ppt.	Brown ppt. with acetic acid.
Orange powder; yellow solu- tion.	Redder.	Brown ppt.	Red.	Brown ppt.	. . .
Red powder; orange solu- tion.	No change.	Violet ppt.	Brown.	Red ppt.	. . .
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	. . .
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	. . .
Brown powder; red solution in hot water.	Red ppt.	Brown ppt.	Blue.	Brown ppt.	Violet ppt. with acetic acid. Precipitated by magenta.
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Soluble in alco- hol.
Orange powder; orange solu- tion.	No change.	Brown ppt.	Blue.	Brown ppt.	Soluble in alco- hol.
Black powder; violet solu- tion.	No change.	Violet ppt.	Blue.	Violet.	. . .

COMMERCIAL NAME.	FORMULA.	REMARKS.
Direct Red.	$C_6H_2 \begin{cases} (2)CH_3 \\ (5)OC_2H_5 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ C_6H_4-N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic acid.
From Tolidine. Cotton Red.	$C_6H_3 \begin{cases} (2)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic acid.
Azo Blue.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.
Congo Corinth B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)OH \\ (4)SO_3Na \end{cases} \end{cases}$	From N W acid.
Benzopurpurin 4 B. Eclipse Red. Imperial Red. Victoria Red.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \end{cases}$	From naphthionic acid.
Benzopurpurin 6 B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (5)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (5)SO_3Na \end{cases} \end{cases}$	From L acid.
Benzopurpurin B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \end{cases}$	From Br acid.
Deltapurpurin 5 B.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (7)SO_3Na \end{cases} \end{cases}$	From δ and Br acids.
Brilliant Congo R.	$C_5H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (3)SO_3Na \\ (6)SO_3Na \end{cases} \end{cases}$	From Br and R acids.
Congo Red 4 R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases} \\ C_6H_3 \begin{cases} (3)CH_3 \\ N=N-(4)C_6H_3 \begin{cases} (1)OH \\ (3)OH \end{cases} \end{cases}$	From naphthionic acid and resorcinol.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red powder; red solution.	No change.	Red ppt.	Violet.	Violet ppt.	Soluble in alcohol. Obsolete.
Red powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	. .
Black powder; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	. .
Black powder; red solution.	Cherry-red.	Violet ppt.	Blue.	Violet ppt.	Bluer solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Brown ppt. with acetic acid.
Red powder; orange solution.	Red.	Blue ppt.	Blue.	Blue ppt.	Blue ppt. with acetic acid.
Brown powder; brown solution.	No change.	Brown ppt.	Blue.	Brown ppt.	Brown solution with acetic acid.
Brown powder; orange solution.	Red ppt.	Brown ppt.	Blue.	Brown ppt.	Precipitated by magenta. Brown solution with acetic acid. $MgSO_4$ ppts. the diamine red present.
Brown powder; red solution.	Orange ppt.	Brown ppt.	Blue.	Black ppt.	Bluer solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Brown ppt. with acetic acid.

Commercial Name.	Formula.	Remarks.
Diamine Blue 3 B.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.$	From H acid.
Diamine Blue B X.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.$	From N W and H acids.
Hessian Brown M M.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_6H_2\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(3)OH\\(4)N=N-(1)C_6H_4(4)SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_6H_2\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(3)OH\\(4)N=N-(1)C_6H_4(4)SO_3Na\end{matrix}\right.$	From Resorcin yellow.
Benzo Black Blue R.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(4)C_{10}H_6(1)N=N-(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$	From N W acid.
Direct Gray B.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(OH)_2\\CO_2Na\\SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(OH)_2\\CO_2Na\\SO_3Na\end{matrix}\right.$	. . .
Direct Blue R.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(OH)_2\\CO_2Na\\SO_3Na\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right.$	. . .
Azo Black Blue.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_3\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(1)C_6H_3\end{matrix}\right.\left\{\begin{matrix}(2)NH.C_6H_5\\(4)OH\end{matrix}\right.$	. . .
Oxamine Blue 3 R.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_4\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(3)SO_3Na\\(6)NH_2\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$	From N W acid.
Azo Corinth.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_2\end{matrix}\right.\left\{\begin{matrix}N=N-C_{10}H_6.SO_3Na\\OH\\OH\end{matrix}\right.$ $\dot{C}_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_2\end{matrix}\right.\left\{\begin{matrix}OH\\NH_2\\SO_3Na\end{matrix}\right.$	From naphthionic acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Gray powder; violet solution.	No change.	Violet ppt.	Blue.	Violet ppt.	. . .
Blue powder; violet solution.	Redder.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Brown powder; brown solution.	Redder.	Brown ppt.	Black.	Brown ppt.	Soluble in alcohol.
Black powder; violet solution.	Blue ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Black powder; violet solution in hot water.	Redder.	Gray ppt.	Blue.	Gray ppt.	Shades are fast to light.
Black powder; violet solution.	Redder.	Violet ppt.	Blue.	. .	. . .
Brown powder; violet solution.	. .	Violet ppt.	Blue.	Violet ppt.	Direct dye for cotton.
Violet powder, violet solution.	Violet ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Brown powder; brown solution.	Violet.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Azo Orange R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_{10}H_6 \begin{cases} NH_2 \\ SO_3Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_6H_3OH \end{cases}$ $C_6H_3 \begin{cases} N=N-C_6H_3OH \\ (3)CH_3 \end{cases} CH_2$ $C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_{10}H_6 \begin{cases} NH_2 \\ SO_3Na \end{cases} \end{cases}$	From naphthionic acid.
Mekong Yellow R.	$C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_6H_3 \begin{cases} OH \\ CO_2Na \end{cases} \end{cases}$ $C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_6H_3OH \end{cases}$ $C_6H_3 \begin{cases} N=N-C_6H_3OH \\ (3)CH_3 \end{cases} CH_2$ $C_6H_3 \begin{cases} (3)CH_3 \\ N=N-C_6H_3 \begin{cases} OH \\ CO_2Na \end{cases} \end{cases}$	From salicylic acid.
From Diamido-stilbene. Stilbene Red.	$CH.C_6H_4-N=N-(1)C_{10}H_4 \begin{cases} (2)NH_2 \\ (SO_3Na)_2 \end{cases}$ $\overset{\parallel}{CH}.C_6H_4-N=N-(2)C_{10}H_5 \begin{cases} (1)NH_2 \\ (4)SO_3Na \end{cases}$	From naphthionic acid.
Brilliant Yellow.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_6H_4(4)OH \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_6H_4(4)OH \end{cases}$	From phenol.
Polychromine B.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_6H_4(4)NH_2 \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_6H_4(4)NH_2 \end{cases}$	. . .
Chrysophenine.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(4)C_6H_4(1)OC_2H_5 \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(4)C_6H_4(1)OC_2H_5 \end{cases}$	From Brilliant Yellow.
Hessian Purple N.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)NH_2 \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)NH_2 \end{cases}$	. . .
Brilliant Hessian Purple.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ (6)SO_3Na \end{cases} \end{cases}$	. . .
Hessian Purple B.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ SO_3Na \end{cases} \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ SO_3Na \end{cases} \end{cases}$	From β acid.
Hessian Purple D.	$CH.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ SO_3Na \end{cases} \end{cases}$ $\overset{\parallel}{CH}.C_6H_3 \begin{cases} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \begin{cases} (2)NH_2 \\ SO_3Na \end{cases} \end{cases}$	From γ acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red powder; orange solution.	Redder.	Gray ppt.	Blue.	Gray ppt.	Direct dye for cotton.
Brown powder; brown solution.	Redder.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.
Brown powder; red solution.	No change.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol.
Brown powder; orange solution.	Redder.	Violet ppt.	Violet.	Violet ppt.	Precipitated by magenta.
Brown powder; orange solution.	No change.	Black ppt.	Violet.	Black ppt.	Yields ingrain colors.
Orange powder; orange solution.	Yellow.	Brown ppt.	Violet.	Blue ppt.	. . . .
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Violet ppt. with acetic acid. Precipitated by magenta.
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol.
Brown powder; red solution.	Violet ppt.	Black ppt.	Violet.	Brown ppt.	. . .
Black powder; orange solution.	Bluer.	Brown ppt.	Violet.	Brown.	. . .

COMMERCIAL NAME.	FORMULA.	REMARKS.
Hessian Yellow.	$CH.C_6H_3 \left\{ \begin{array}{l} (2)SO_3Na \\ N=N-C_6H_3 \end{array} \right\} \left\{ \begin{array}{l} (1)OH \\ (2)CO_2H \end{array} \right.$ $CH.C_6H_3 \left\{ \begin{array}{l} (2)SO_3Na \\ N=N-C_6H_3 \end{array} \right\} \left\{ \begin{array}{l} (1)OH \\ (2)CO_2H \end{array} \right.$	From salicylic acid.
Hessian Violet.	$CH.C_6H_3 \left\{ \begin{array}{l} (2)SO_3Na \\ N=N-(4)C_{10}H_6(1)NH_2 \end{array} \right.$ $CH.C_6H_3 \left\{ \begin{array}{l} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{array} \right.$	. . .
Diamido-azoxy derivatives. St. Denis Red.	$O \left< \begin{array}{l} N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-C_{10}H_5 \end{array} \right\} \left\{ \begin{array}{l} OH \\ SO_3Na \end{array} \right. \\ N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-C_{10}H_5 \end{array} \right\} \left\{ \begin{array}{l} OH \\ SO_3Na \end{array} \right. \end{array} \right.$	From N W acid.
Acid Milling Scarlet.	$O \left< \begin{array}{l} N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-(2)C_{10}H_5 \end{array} \right\} \left\{ \begin{array}{l} (1)OH \\ (4)SO_3Na \end{array} \right. \\ N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-(1)C_{10}H_4 \end{array} \right\} \left\{ \begin{array}{l} (2)OH \\ (3)SO_3Na \\ (6)SO_3Na \end{array} \right. \end{array} \right.$	From R acid.
Rock Scarlet Y S.	$O \left< \begin{array}{l} N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-(2)C_{10}H_5 \end{array} \right\} \left\{ \begin{array}{l} (1)OH \\ (4)SO_3Na \end{array} \right. \\ N-C_6H_3 \left\{ \begin{array}{l} CH_3 \\ N=N-(1)C_{10}H_6(2)OH \end{array} \right. \end{array} \right.$	From N W acid.
From amido- acetanilide. Salmon Red.	$OC \left< \begin{array}{l} NH.C_6H_4-N=N-C_{10}H_5 \left\{ \begin{array}{l} (1)NH_2 \\ (4)SO_3Na \end{array} \right. \\ NH.C_6H_4-N=N-C_{10}H_5 \left\{ \begin{array}{l} (1)NH_2 \\ (4)SO_3Na \end{array} \right. \end{array} \right.$	From naphthionic acid.
Cotton Yellow G.	$OC \left< \begin{array}{l} NH.C_6H_4-N=N-C_6H_3 \left\{ \begin{array}{l} (1)OH \\ (2)CO_2Na \end{array} \right. \\ NH.C_6H_4-N=N-C_6H_3 \left\{ \begin{array}{l} (1)OH \\ (2)CO_2Na \end{array} \right. \end{array} \right.$	From salicylic acid.
Cotton Scarlet.	$CH \left\{ \begin{array}{l} C_6H_2(CH_3)_2-N=N-C_{10}H_4 \left\{ \begin{array}{l} OH \\ (SO_3Na)_2 \end{array} \right. \\ C_6H_5 \\ C_6H_2(CH_3)_2-N=N-C_{10}H_4 \left\{ \begin{array}{l} OH \\ (SO_3Na)_2 \end{array} \right. \end{array} \right.$	From R acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARAC-TERISTICS.
	With Caustic Soda.	With Hy-drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Yellow powder; yellow solu-tion.	Red.	Black ppt.	Violet.	Black ppt.	. . .
Black powder; violet solu-tion.	Bluer.	Blue ppt.	Blue.	Violet ppt.	. . .
Red powder; red solution.	Red ppt.	Red ppt.	Red.	Red ppt.	Soluble in alco-hol.
Red powder; red solution.	Orange ppt.	No change.	Red.	Scarlet.	Shades are fast to milling.
Red powder; red solution.	Orange ppt.	Scarlet ppt.	Violet.	Scarlet ppt.	Shades are fast to milling.
Brown powder; orange solu-tion.	No change.	Violet ppt.	Red.	Violet ppt.	. . .
Yellow powder; yellow solu-tion.	Orange.	Brown ppt.	Orange.	Violet ppt.	. . .
Brown powder; red solution.	Redder.	No change.	Red.	Orange.	. . .

The preceding tables show the constitution and reactions of the more important dyes from benzidine and its analogues.

The coloring matters named in the foregoing tables may be distinguished from all other azo-dyes by heating a piece of unmordanted cotton in the aqueous solution. The cotton is then removed to a warm solution of soap, which will strip the dye from the fibre unless the color be derived from benzidine or an analogous diamine.

The dyes from benzidine, etc., can be fixed on silk from a bath containing soap and phosphate of sodium; and mixed silk and cotton goods take the color well and evenly.

The benzidine dyes act as mordants to the basic aniline dyes, a fact of which the practical application is evident. In general, the benzidine dyes are not fast to light, and have the objectionable property of ''bleeding.'' Most of them are also sensitive to the action of acids.

The following is a detailed description of the more important of the dyes from benzidine and its analogues:—

Chrysamine G, or FLAVOPHENINE, is produced by the action of tetrazo-diphenyl chloride on sodium salicylate. It is sparingly soluble in cold but readily in boiling water. The solution has an orange color, changed by caustic soda to an orange-red, from which acids precipitate t e t r a z o d i p h e n y l - d i s a l i c y l i c a c i d in orange flakes soluble in ether.[1] Chrysamine is very sensitive to the action of copper compounds, its color being darkened to a brown. For this reason it should not be brought in contact with copper vessels while dyeing. Chrysamine differs from most of the other benzidine dyes in that its shades are very fast to light and soap.

Congo-Red forms a brownish-red powder, readily soluble in water to produce a blood-red solution. Very small quantities of dilute acids turn the liquid to a beautiful blue, a precipitate of the free s u l p h o n i c a c i d being formed in strong solutions. Alkalies restore the red color, and salts of neutral constitution, such as alum,[2] ferrous sulphate, cupric sulphate, etc., do not act

[1] Chrysamine is probably the only commercial azo-dye which is extracted by agitating its acidulated aqueous solution with ether.

[2] The naphthol-azo colors have been employed in the coloration of sand for experimental purposes in hydraulic engineering, where it is desirable to use sand of different colors, which colors must resist the action of water and friction fairly well. The dyes are dissolved in caustic soda, and the sand is treated with the diluted solution.

as acids.   Hence it has been proposed to employ congo-red as an indicator of neutrality, but it has been shown by R. T. T h o m p - s o n (*Jour. Soc. Chem. Ind.*, vi. 195) that its delicacy has been overrated.[1]   While not wholly unaffected by weak acids, such as carbonic and sulphydric, it fails to indicate the presence of acetic acid in presence of twelve times the quantity of sodium acetate.[2] Congo-red dissolves in strong sulphuric acid with slate-blue color, which is not changed by dilution.   Congo-red dyes cotton a bright crimson-red, but the color is far from permanent.   Exposure to light and air for a short period dulls the color, which is restored to its original brightness on soaping.   After longer exposure to light, the color cannot thus be restored.   On wool the color is rather more scarlet, brighter, and more stable than on cotton.

Benzopurpurin 4 B is the next higher homologue of congo-red. It forms a dark brownish-red powder, soluble in water with orange-red color, which is unchanged by alkalies.   From strong solutions, dilute acids throw down the free s u l p h o n i c a c i d as a reddish-brown precipitate resembling ferric hydroxide.   In a hot bath containing soap or alkaline carbonate, benzopurpurin dyes cotton a fine scarlet.   The color is almost unaffected by dilute acids, and is much faster to light than congo-red.

BENZOPURPURIN B is isomeric with the last named dye, and is prepared by the reaction of diazotized tolidine on β-naphthyl-amine-sulphonic acid[3] in presence of alkali.   It dyes cotton a color approaching a turkey-red in tint of brilliancy.   Acids turn the dyed fibre blue, the color being restored by alkalies or washing.[4]

[1] R. T. Thompson finds that congo-red is incapable of indicating with certainty the presence of 0.2 per cent. of sulphuric acid in alum, or even of giving a trust-worthy reaction with 0.5 per cent.

[2] Congo-red is useful for titrating aniline and toluidine in the residual liquors from aniline works.   Congo-red paper, blued by acid, is reddened by aniline and alkaloids in general.

[3] The sulphonic acid is the so called β-m o d i f i c a t i o n, obtained (mixed with the a- and γ-isomerides) by heating β-naphthylamine with 8 parts of sulphuric acid (96–97 per cent. of H_2SO_4) to 100°–105° C. for six hours, or by heating Schäffer's β-naphthol-sulphonic acid with ammonia.

[4] According to S t o r c h benzopurpurin B is a superior indicator to congo-red, it being the most sensitive indicator for alkalies known.   The slight trace of ammonia in the atmosphere is sufficient to change the color of paper impregnated with a solution of benzopurpurin B from bluish-violet to red.   It may be used for estimating ammonia in the presence of pyridine; as titration with hydrochloric acid will show the total base, and a second titration with litmus, on which pyri-dine has no effect, will show the ammonia present.

DELTAPURPURIN G is isomeric with congo-red, and like its homologue *Deltapurpurin 5 B* is obtained by the use of the so-called δ-modification of β-naphthylamine-sulphonic acid.[1] The deltapurpurins dye cotton a bright scarlet. Deltapurpurin 5 B is distinguished from its isomer *diamine red 3 B*[2] and from *delta-purpurin 7 B* by not being precipitated from its aqueous solution by acetic acid, and by forming a soluble calcium salt.

AZO-BLUE is closely related in constitution to benzopurpurin, the two NH_2 groups of the latter being replaced by two of OH. In the concentrated solution, hydrochloric acid produces a violet-blue precipitate, but dilute acetic acid occasions no change. In a boiling hot bath containing soap and sodium phosphate, azo-blue dyes cotton a violet-blue color, fast to soap, and unaffected by acids.

Benzo-azurin R forms a dark blue (almost black) powder, with a slight bronze reflex. Benzo-azurin dyes cotton a dark shade of blue. The color is remarkably fast to light, and unaffected by acids, but is reddened by alkalies.

BENZO-AZURIN G differs from the last named dye in not being precipitated from its solution by dilute acids, the color being simply darkened. On cotton it dyes a brighter color than the last, and on wool it gives a pleasant and useful shade of violet.

Brilliant Yellow forms a readily soluble brown powder. The solution is orange, changed to scarlet by alkalies, and gives a blue-black precipitate with dilute acids. It dyes cotton and wool a very bright orange shade of yellow, quite fast to light. Acids change the color of the fibre to blue, and alkalies redden it; soaping turns it a shade redder, but there is no bleeding.

On treating brilliant yellow with soda it forms a red basic salt, and on ethylating this body it is converted into

Chrysophenine. This forms a light orange powder, partially

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[1] The β-n a p h t h y l a m i n e - δ-s u l p h o n i c a c i d, used for the production of the *deltapurpurins*, is prepared by heating β-naphthylamine sulphate with 5 or 6 parts of strong sulphuric acid (1.845 specific gravity) to 150° C. for 1½ hour. The α- and γ- sulphonic acids of β-naphthylamine are said to be transformed into the β-modification by this treatment.

[2] Prepared by acting on diazotized tolidine in alkaline solution with β - n a p h - t h y l a m i n e - F - s u l p h o n i c a c i d. This is prepared by fusing the sodium salt of α-naphthalene-disulphonic acid with four times its weight of 50 per cent. caustic soda at 200° C., until dioxynaphthalene begins to be formed. β-naphthol-F-sulphonic acid is formed, and on heating this with ammonia under pressure the corresponding amido-acid is obtained.

soluble in water.   The solution is unchanged by alkalies, but gives
a dark brownish-red precipitate with acids.   In a neutral bath it
dyes both wool and cotton a bright yellow, unaffected by dilute
acids, alkalies, or soaps.

Azarine R is a coloring matter of peculiar constitution, being
represented by the following formula:—

$$SO_2 \begin{cases} C_6H_3 \begin{cases} OH \\ N = N - C_{10}H_6.OH \end{cases} \\ C_6H_3 \begin{cases} OH \\ N = N - C_{10}H_6.OH \end{cases} \end{cases} + 2NH_4HSO_3.$$
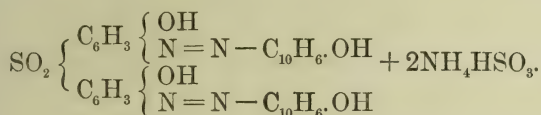
It is produced by diazotizing diamido-dihydroxybenzosulphone,
$SO_2(C_6H_3(OH).NH_2)_2$, and causing the product to react with beta-
naphthol.   The azo-compound formed is then treated with acid
sulphite of ammonium or sodium, which forms a compound of
the nature shown above.   The employment of azarine is an appli-
cation of the fact that many azo-compounds which are themselves
insoluble combine with the acid sulphites of the alkali-metals to
form compounds which are soluble in water, and unaffected by di-
lute acids, but which under the influence of heat are decomposed
into a bisulphite of alkali-metal and an insoluble azo-dye.   The
reaction is capable of being used in calico-printing.

Azarine occurs in commerce in the form of an orange-yellow
paste, closely resembling alizarin paste.   It is sparingly soluble in
water, but dissolves readily in alkalies with bluish-violet color.
The aqueous solution is yellow, and yields an orange-yellow pre-
cipitate with hydrochloric acid, and with caustic soda a violet pre-
cipitate, which dissolves to a red solution on heating.   On heating
the paste, sulphur dioxide is evolved, and the color changes to
scarlet.   Strong sulphuric acid dissolves azarine paste with ma-
genta-red color, a reddish-brown precipitate being formed on dilu-
tion.   Azarine forms alumina-lakes of a fine red color with a shade
of violet.   It is very fast to soap and chlorine, but is affected by
light.

General Analytical Reactions of Azo-Dyes.

The great majority of the azo-dyes are sulphonated, and more
or less soluble in water.   In no case is a sulphonated dye removed
from its aqueous solution by agitation with ether, whether the
liquid be alkaline or acid.   There are a limited number of unsul-
phonated azo-dyes, such as *chrysoïdine* and *bismarck brown*, from

which the free base may be extracted by agitating the alkaline solution with ether. *Chrysamine*, on the other hand, is an unsulphonated azo-dye of acid character, and is removed from its acidulated aqueous solution on agitation with ether.

The azo-dyes are stated to be non-poisonous. Out of those which have been examined, only two have proved to be poisonous in a slight degree, namely: metanil yellow and orange II. On addition of hydrochloric acid to the concentrated aqueous solution of a hydroxyazo-dye, a precipitate is usually produced if the coloring matter contain only one SO_3H group, as in that case the free sulphonic acid often is insoluble or sparingly soluble in water. But when the free acid contains two sulphonic groups it is soluble in water, and hence is not precipitated when the solution of the dye is acidulated.[1] Tropæolin 3 O gives a purple precipitate soluble in excess of hydrochloric acid, and some of the scarlets behave similarly.

The caustic alkalies and ammonia do not usually produce a precipitate in solutions of the sulphonated azo-dyes; but they often change the color, owing to the replacement of the hydrogen of the hydroxyl groups.[2]

The concentrated solutions of many of the azo-dyes are precipitated by barium and calcium chlorides, and in some cases the reactions are of analytical interest. The azo-dyes as a class are remarkable for the striking colorations produced when the solid substance is treated with concentrated sulphuric acid, as was first pointed out by J. S p i l l e r (*Chem. News*, xlii. 191). To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube or porcelain crucible with strong sulphuric acid. Very frequently, useful information can be gained by observing the spectrum of the colored liquid obtained. In the case of the tetrazo-dyes the color of the solution in strong sulphuric acid is an important indication of the constitution of the coloring matter (see page 180).

Among the most characteristic reactions of the azo-dyes is their

[1] This statement does not apply to the benzidine dyes, almost all of which are precipitated by dilute acid.

[2] Thus a mere trace of alkali changes the dilute solution of mandarin from yellow to crimson (exactly the opposite being true of methyl-orange). Scarlets G and R and crocein and biebrich scarlets show a similar reaction, but are far less sensative than mandarin. Ammonia is almost without action on solutions of scarlets 2 R and 3 R.

behavior with reducing agents, the most generally suitable reagent for the purpose being hydrochloric acid and zinc or solution of stannous chloride.[1] Thus the amido-azo-compounds are split up into a p r i m a r y a m i n e and p a r a - d i a m i n e, amido-azobenzene yielding aniline and paraphenylene-diamine (para-diamidobenzene):—$C_6H_5N:N.C_6H_4.NH_2 + 2H_2 = C_6H_5.NH_2 + C_6H_4(NH_2)_2$.

Similarly, when helianthin is reduced it yields the ammonium salt of s u l p h a n i l i c a c i d (amidobenzene-sulphonic acid) and d i m e t h y l - p a r a d i a m i d o b e n z e n e:—

$$C_6H_4(SO_3NH_4).N:N.C_6H_4N.(CH_3)$$
$$= C_6H_4(SO_3NH_4)NH_2 + H_2N.C_6H_4.N(CH_3)_2.$$
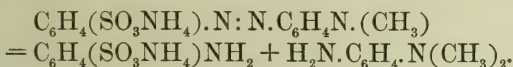
The best way of affecting this reduction is to heat the helianthin on the water-bath with ammonium sulphide until the orange color disappears.   The ammoniacal liquid is agitated with ether, and the ethereal layer separated from the aqueous liquid containing ammonium sulphanilate.   The ethereal solution agitated with moist hydrated oxide of lead (to get rid of sulphide), filtered, and evaporated, leaves free dimethyl-paradiamido-benzene.   This base melts at 41° and boils at 257°.   It forms asbestos-like needles, which when pure are unchanged on exposure to air, but otherwise turn red or violet.   It is readily soluble in water, alcohol, chloroform, and benzene, but less so in ether or petroleum ether.   It may be purified by conversion into the sulphate and crystallizing the salt from absolute alcohol.   On treating the free base or a salt with a hydrochloric acid solution of sulphuretted hydrogen, and then adding ferric chloride till the odor of sulphuretted hydrogen has disappeared, a splendid blue coloration is produced, *methylene blue* being formed.

An acid solution of stannous chloride reduces the hydroxyazo-dyes in a similar manner, the products being a primary amine and an amidophenol.   Thus oxyazobenzene yields a n i l i n e, $C_6H_5NH_2$, and p a r a - a m i d o p h e n o l, $C_6H_4(NH_2)OH$.   Mandarin splits up similarly into s u l p h a n i l i c a c i d, $C_6H_5(SO_3H)NH_2$, and

[1] O. N. Witt (*Ber*, 1888, p. 3468) gives the following method of carrying out this reduction : One gram of dyestuff is dissolved in the smallest quantity of boiling water (generally 10–20 parts), the little flask is removed from the flame and 6 c.c. of tin solution are added, prepared by dissolving 40 gms. tin in 100 c.c. of pure hydrochloric acid (sp. gr. 1.19).   The reduction is usually accomplished in a few minutes.   If the amido-naphthol or naphthylene-diamine sulphonic acid does not separate out on cooling, a saturated salt solution, or other precipitant, is added.

a m i d o b e t a n a p h t h o l, $C_{10}H_5(NH_2)OH$. When the naphthol group is sulphonated, the amidonaphthol-sulphonic acid decomposes into amido-naphthol and free sulphuric acid. Thus xylidine-red is decomposed as follows:—$C_6H_3(CH_3)_2N:N:C_{10}H_4.$ $(SO_3Na_2)OH + 2H_2O = C_6H_3(CH_3)_2NH_2 + C_{10}H_6(NH_2).OH + 2Na-HSO_4.$ With an alkaline reducing agent, such as ammonium sulphide or zinc and ammonia, the amidonaphthol-disulphonic acid does not undergo decomposition.

Secondary azo-dyes split up in a similar manner under the action of reducing agents. Thus with metallic tin or stannous chloride and hydrochloric acid, biebrich scarlet yields sulphanilic acid, paradiamido-benzene, and amidonaphthol. With an alkaline reducing agent, such as zinc and ammonia, biebrich scarlet undergoes a modified decomposition, resulting in the formation of amidohydrazo-benzene sulphonate and amido-naphthol, thus:—

$$C_6H_4(SO_3Na).N:N.C_6H_4.N:N.C_{10}H_6.OH + 3H_2$$
$$= C_6H_4(SO_3Na).NH:NH.C_6H_4.NH_2 + C_{10}H_6(NH_2).OH.$$
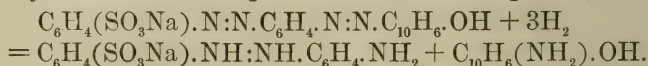
On exposing the decolorized liquid to the air it rapidly acquires a yellow color, from the production of sodium amido-azobenzene-sulphonate or *acid yellow*. Other tetrazo-dyes behave similarly.

Congo-red, the type of the benzidine dyes, on reduction yields benzidine and a diamidonaphthalene-sulphonic acid, $C_{10}H_5(SO_3H)^a$ $(NH_2)^a(NH_2)^\beta$.

It will be seen that the investigation of the behavior of the azodyes with reducing agents affords a most valuable means of recognizing them and ascertaining their constitution. The bases resulting from the treatment can be extracted from the alkaline liquid with ether,[1] and if more than one be produced they can be separated by fractional distillation or crystallization of their salts. The isolation and identification of the amidophenols is very difficult, especially as some of them are very readily affected by air. Hence it is preferable, when it is desired to obtain them in a pure state, to evaporate the neutralized solution to dryness, and heat the residue with anhydrous sodium carbonate.

The following table gives some of the leading characters of certain of the bases produced by the reduction of commercial azo-dyes:—

[1] Whenever an amidonaphthol-sulphonic acid is a product of the reduction, it decomposes into an amidonaphthol and free sulphuric acid, if an acid reducing agent be employed; but is not decomposed, and hence does not pass into the ether, when ammonium sulphide is used as the reducing agent.

NAME.	FORMULA.	MELTING POINT °C.	BOILING POINT °C.	OTHER CHARACTERS.
Aniline. Amidobenzene. Phenylamine.	$C_6H_5.NH_2$	–8	183.7	Sparingly soluble. Violet color with bleaching solution.
Ortho-toluidine. Ortho-amido-toluene.	$C_6H_4 \begin{cases} (1)CH_3 \\ (2)NH_2 \end{cases}$	Below–20	198	Brown color with bleaching solution. Color soluble in ether, and changed to pink by dilute acetic acid.
Paratoluidine. Paramidotoluene.	$C_6H_4 \begin{cases} (1)CH_3 \\ (4)NH_2 \end{cases}$	45	198	White, crystalline. No reaction with bleaching powder. Dissolved in strong H_2SO_4 and nitric acid added, gives blue, changing to red.
Alpha-naphthyl-amine. Alpha-amido-naphthalene.	$C_{10}H_7.NH_2$	50	300	Characteristic and presistent odor. Turns violet on exposure. $FeCl_3$ and other oxidizing agents give azure-blue precipitate.
Diphenylamine.	$(C_6H_5)_2.NH$	54	110	Nearly insoluble plates. Deep blue color on adding to its solution in pure sulphuric acid a trace of nitrous sulphuric acid.
Para-amido-di-phenylamine.	$NH_2.C_6H_4.NH.C_6H_5$	61	. .	Small lustrous plates, becoming green in the air. $FeCl_3$ gives a red color, changing to green, and on concentration a green precipitate, soluble in H_2SO_4 with a carmine-red color.
Paraphenylene-diamine. Paradiamido-benzene.	$C_6H_4:(NH_2)_2$	140	267	Sparingly soluble tablets. Oxidized to quinone by MnO_2 and dilute H_2SO_4.
Dimethyl-para-diamido-benzene.	$C_6H_4 : \begin{cases} NH_2 \\ N(CH_3)_2 \end{cases}$	41	257	Easily soluble. Gives methylene blue with a solution of H_2S in hydrochloric acid.
Para-amidophenol	$C_6H_4 \begin{cases} (1)OH \\ (4)NH_2 \end{cases}$	184 decomposing.	. .	Colorless plates, rapidly turning brown. Alkaline solution becomes violet on exposure, and yields quinone with oxidizing agents. With bleaching solution, a violet-color, changing to green.
a-Amido-alpha-naphthol.	$C_{10}H_6 \begin{cases} (1)OH \\ (8)NH_2 \end{cases}$	. .	. .	On agitating the alkaline solution with air, a dirty green color is produced, changing to yellow. With bromine water, yellow-white crystalline precipitate. With oxidizing agents yields the theoretical amount of a-naphtha-quinone.
β-Amido-alpha-naphthol.	$C_{10}H_6 \begin{cases} (1)OH \\ (2)NH_2 \end{cases}$	. .	. .	On agitating the alkaline solution with air, permanent grass-green color, and green scum soluble in alcohol to pure green solution. Br and $FeCl_3$ give yellowish or green precipitate, and no naphtha-quinone is formed on heating.
Amido-resorcinol.	$C_6H_3(OH)_2.NH_2$	. .	. .	Flat plates turning green in the air. NaHO gives deep blue color, changing to green and brown. $FeCl_3$ gives deep brown color, and then nearly black precipitate.

5. Oxyketones.

The oxyketone colors are chiefly derivatives of anthracene. They are limited in number, and even of these few have any practical value as dyes. They differ materially from the coal-tar dyes hitherto considered, though presenting considerable resemblance among themselves, and several members of the group are coloring matters of the first importance.[1]

The starting point in the production of a l i z a r i n and allied coloring matters is commercial a n t h r a c e n e, containing from 50 to 55 per cent. of the pure hydrocarbon, $C_{14}H_{10}$, or sometimes a purer product, obtained by sublimation, is employed.[2]

This is suspended in water and treated with $1\frac{1}{2}$ times its weight of potassium bichromate and an equivalent quantity of sulphuric acid, when the anthracene is converted into a n t h r a q u i n o n e, $C_{14}H_8O_2$. The product is separated by filtration, dried, treated with strong sulphuric acid (sp. gr. 1.84), and the mixture heated to 105°–110° C. The black product is treated with steam, which is absorbed by the sulphuric acid, and as the dilution proceeds the anthraquinone crystallizes out. Boiling water is then added, and the product well washed with hot water and solution of soda to remove associated organic acids, after which it is further purified by sublimation or distillation in a current of superheated steam. The product contains from 96 to 98 per cent. of real anthraquinone, and forms golden-yellow prismatic needles, melting at

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[1] The money value of artificial alizarin and the allied colors is more than one-third of that of the total coal-tar dyes, and the price of alizarin, compared tinctorially, is not more than one-fourth of what it was in the form of madder and garancine.

[2] Commercial anthracenes are divided into two classes, known as A and B quality. The nature of the impurities present in the latter is not thoroughly understood, though of these β-methylanthracene is frequently one. In the usual process this yields first its quinone and finally methyl alizarine, which dye shades of a duller character and less fast than the true alizarins.

Paraffin, if present in anthracene, may be detected by heating the sample with sulphuric acid at 100°. A method for determining the amount of paraffin is based on the fact that all of the constituents of crude anthracene with the exception of paraffin are soluble in fuming nitric acid. About 2 gms. of crude anthracene is placed in a flask with 25 c.c. of fuming nitric acid; the acid being added gradually while the flask is kept in ice-water. After all the anthracene has dissolved, the flask is heated on a water bath until the paraffin is melted. The solution is then filtered through an asbestos filter, the paraffin is washed with fuming nitric acid, and finally dissolved in warm ether, dried, and weighed.

273° C., insoluble in water, highly stable and indifferent, and unacted on by bases or dilute acids.[1]

[1] For the analysis of crude anthraquinone two distinct tests are necessary. (1.) Determination of the anthraquinone it is capable of yielding. (2.) Determination of the anthraquinone present in the crude product. The former operation is simply an anthracene test by Luck's method, whilst in carrying out the second test, 10 grms. of the finely powdered sample are treated with 10 to 15 grms. of sulphuric acid at 100° for one hour. The mass is then boiled out in water and the anthraquinone filtered, washed, dried, and weighed. To ascertain its purity 1 grm. is treated with 10 grms. of sulphuric acid containing 10 per cent. of sulphuric anhydride at 100° for one hour. It is then placed in a damp atmosphere for 12 hours and allowed to crystallize. After the addition of water the crystals are collected, washed with water, dilute alkali, again with water, dried and weighed. From the difference between the result of this analysis and that of the Luck's method, the percentage of unoxidized anthracene can be easily calculated.

The method employed for the analysis of purified anthraquinone consists in heating 1 grm. with 10 grms. of sulphuric acid containing 10 per cent. of sulphuric anhydride, the course of procedure being identical with the second portion of the anthracene test. The grey or green tinge of anthraquinone purified with sulphuric acid is due to the presence of a dark-colored amorphous product, which is insoluble in the usual solvents and contains nitrogen, originating possibly from the carbazol or other nitrogenous impurities existing in crude anthracene. Methyl anthraquinone being moderately soluble in boiling dilute sulphuric acid, especially if this contains other sulphonic acids in solution, a purer anthraquinone is obtained by filtering the purified product from the acid solution of sulphonated hydrocarbons at an elevated temperature.

For the final purification of anthraquinone it is either re-purified with sulphuric acid at 100°, or sublimed by means of superheated steam, or recrystallized from some suitable solvent. The estimation of pure anthraquinone is carried out in the same way as that employed with the purified product. Frequently, however, its valuation in this manner is accompanied by a second determination, in which the full anthracene test is used.

Sodium anthraquinonemonosulphonate is produced on a large scale, in an almost chemically pure condition, and no analysis is required beyond a determination of the moisture present. The filtrate and washings from this salt consist chiefly of a mixture of the two disulphonic acids. If neutralized and converted into color no further valuation is required, for knowing the weight of anthraquinone originally employed in the sulphonation, and also the anthraquinone value of the sodium mono-salt and unattacked anthraquinone, this value can be at once determined by difference. The anthraquinone unattacked during the sulphonating operation is mostly weighed and sampled in the wet condition, the amount of moisture being then determined. For its analysis 1 grm. of the dried sample is dissolved in glacial acetic acid and the solution treated with chromic acid (one-half the usual quantity) as in the first portion of the anthracene test.

Sodium anthraquinone disulphonates. If the resulting solution of the α- and β-disulphonic acids be at once neutralized and converted into color, no analysis is necessary, for as a rule the whole of the anthraquinone is sulphonated. If, however, a separation of the acids be desired, one of the resulting sulphonates must

Anthraquinone has a constitution expressed by the formula $C_6H_4 : \left\{ \begin{matrix} CO \\ CO \end{matrix} \right\} : C_6H_4.$ When treated with fuming sulphuric acid containing 50 per cent. of the anhydride, it yields a n t h r a - q u i n o n e - m o n o s u l p h o n i c acid, the sodium salt of which if fused for several days at 180° to 200° C. with caustic soda, and sufficient potassium chlorate or nitrate to prevent reduction by the hydrogen evolved, yields s o d i u m a l i z a r a t e,[1] thus:—

$$C_6H_4 : C_2O_2 : C_6H_3SO_3Na + 3H(ONa) = C_6H_4 : CO_2 : C_6H_2(ONa)_2$$
$$+ Na_2SO_3 + H_2O + H_2.$$
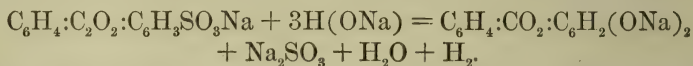
On dissolving the melt in water and adding hydrochloric acid, free *alizarin*, or o r t h o - d i h y d r o x y - a n t h r a q u i n o n e, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$, is precipitated.

If, in the treatment of the anthraquinone with fuming sulphuric acid, an excess of the reagent be employed, instead of the mono-sulphonic acid a *beta*-disulphonic acid is the chief product; but if the temperature be increased to 180°–185°, the isomeric *alpha*-disulphonic acid is the more abundant.[2]

On fusing the alpha-disulphonic acid of anthraquinone with caustic soda, it is converted into the sodium salt of a n t h r a f l a v i c a c i d, while the beta-acid when thus treated yields the isomeric body i s o - a n t h r a f l a v i c acid. Both these substances are dihydroxyanthraquinones, like alizarin, and dissolve in alkalies with yellow color, but have no dyeing properties. If the fusion of the alpha- and beta-disulphonic acids of anthraquinone with caustic soda be conducted in presence of an oxidizing agent, the products are the sodium salts of f l a v o p u r p u r i n and a n t h r a - p u r p u r i n respectively. Both these bodies are valuable dye-matters, and have the constitution of t r i h y d r o x y - a n t h r a - q u i n o n e s, $C_6H_4 : C_2O_2 : C_6H(OH)_3$, the difference between them being due to the positions of the hydroxyl groups. They are both

be examined. For its analysis, the amount of moisture is first determined and the dried residue subsequently incinerated with the aid of ammonium nitrate or sulphuric acid. The loss by ignition multiplied by $1·526 \times 100$ and divided by the weight of dry substance gives the percentage of the pure salt in the dry sub-stance. *Perkin* (*Jour. Soc. Dyers, etc.*, 1897, 81.)

[1] If the fusion be conducted in the absence of air, and no oxidizing agent be added, the sodium compound of m o n o - h y d r o x y a n t h r a q u i n o n e is formed.

[2] On converting the mixed product into sodium salts and adding dilute sul-phuric acid, the sparingly soluble monosulphonate can be separated from the easily soluble acid sodium salts of the two isomeric disulphonic acids.

isomeric with the natural substance p u r p u r i n, contained in madder, which has been obtained synthetically by oxidizing alizarin in solution in concentrated sulphuric acid. A n t h r a - g a l l o l is a fourth trihydroxy-anthraquinone, obtained by the action of phthalic anhydride on pyrogallol in sulphuric acid solution.

Several t e t r a h y d r o x y a n t h r a q u i n o n e s (*e. g.* anthra-chrysone, hydroxypurpurin, rufiopin) are known, while r u f i - g a l l i c a c i d has the constitution of a h e x a h y d r o x y a n - t h r a q u i n o n e.

The constitution of anthraquinone derivatives is best interpreted by the aid of the '' benzene chain.''
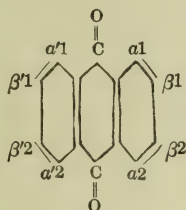
The diagram represents the constitution of anthraquinone, an atom of carbon being situated at each angle, and combined at the α and β positions with an atom of hydrogen. By the replacement of one or more of these hydrogen atoms by a corresponding num-ber of hydroxyl groups, various hydroxy-derivatives of anthra-quinone are obtainable, and their constitution, so far as it is known, will be understood by comparing the following table with the diagram:—

NAME.	FORMULA.	POSITION OF SUBSTITUTED H ATOMS.	MELTING POINT ° C.
ANTHRAQUINONE, ...	$C_{14}H_8O_2=C_6H_4:C_2O_2:C_6H_4$	. .	273
MONOHYDROXYANTHRAQUINONES, .	$C_{14}H_7O_2(OH)$	. .	. .
Erythrohydroxyanthraquinone,	$C_6H_4:C_2O_2:C_6H_3(OH)$	$a1$	. .
Beta-hydroxyanthraquinone, . .	Do.	$\beta1$	323
DIHYDROXYANTHRAQUINONES, . .	$C_4H_6O_2(OH)_2$	. .	. .
Alizarin, ...	$C_6H_4:C_2O_2:C_6H_2(OH)_2$	$a1; \beta1$	289–290
Purpuroxanthin, ...	Do.	$a1; \beta2$	262–263
Quinizarin, ...	Do.	$a1; a2$	194
Chrysazin, ...	$C_6H_3(OH):C_2O_2:C_6H_3(OH)$	$a'1; a1$	191
Anthrarufin, ...	Do.	$a'2; a1$	. .
Anthraflavic acid, ...	Do.	$\beta2; \beta1$	Above 330
Isoanthraflavic acid, ...	Do.	$\beta1'; \beta1$	Above 330
Anthraflavone, ...	Do.	?	291–293
Frangulic acid, ...	Do.	?	252–254
Isoalizarin, ...	Do.	?	. .
TRIHYDROXYANTHRAQUINONES, . .	$C_{14}H_5O_2(OH)_3$	. .	. .
Anthragallol, ...	$C_6H_4:C_2O_2:C_6H(OH)_3$	$a1; \beta1; \beta2$	. .
Purpurin, ...	Do.	$a1; \beta1; a2$	. .
Anthrapurpurin, ...	$C_6H_3(OH):C_2O_2:C_6H_2(OH)_2$	$\beta'1; a1; \beta1$	About 360
Flavopurpurin, ...	Do.	$\beta'2; a1; \beta1$	Above 330
Hydroxychrysazin, ...	Do.	?	. .
TETRAHYDROXYANTHRAQUINONES,	$C_{14}H_4(OH)_4O_2$	. .	. .
Anthrachrysone, ...	$C_6H_2(OH)_2:C_2O_2:C_6H_2(OH)_2$	?	320
Hydroxypurpurin, ...	. . .	?	. .
Rufiopin, ...	. . .	?	. .
HEXHYDROXYANTHRAQUINONES, .	$C_{14}H_2(OH)_6O_2$	. .	. .
Rufigallic acid, ...	$C_6H(OH)_3:C_2O_2:C_6H(OH)_3$	?	. .

By the oxidation of m e t h y l - a n t h r a c e n e, $C_{14}H_9(CH)_3$, a series of products parallel to the above may be obtained. C h r y s o p h a n i c   a c i d, $C_6H_4:C_2O_2:C(CH_3)(OH)_2$ is a dihydroxy-methylanthraquinone, while e m o d i n is a trihydroxy-derivative.

Such of the hydroxy-derivatives of anthraquinone as receive practical application are not known generally by their systematic or descriptive names, but are simply termed " alizarin for reds," " alizarin for blues," &c. Hence it will be convenient to describe fully the characters of true alizarin, and subsequently treat of the various products known in commerce as " alizarin."

Alizarin.   Ortho-dihydroxy-anthraquinone.

$$C_{14}H_8O_4 = C_6H_4 {<}^{CO}_{CO}{>}C_6H_2 \left\{ {}^{(1)OH}_{(2)OH} \right.$$
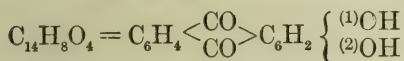
Alizarin exists ready-formed in madder-root (*Rubia tinctorum*), but the proportion of actual alizarin is, except in old roots, small compared with that existing potentially in the form of r u b e r y t h r i c a c i d,[1] a glucoside which on steeping the madder roots in water is resolved, under the influence of a peculiar ferment called e r y t h r o z y m e, into a l i z a r i n and d e x t r o - g l u c o s e, according to the following equation:—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$
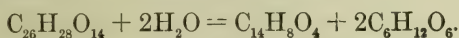
Various methods of accelerating this change have been devised, the most important and rational being to treat the powdered root, previously exhausted with water, with strong sulphuric acid, which splits up the ruberythric acid according to the foregoing equation, without altering the resultant alizarin.   The product thus obtained was called g a r a n c i n e, but the cultivation of madder as a source of alizarine is now almost entirely abandoned, and garancine and similar products have little more than an historical interest.

Alizarin is now manufactured artificially on a very large scale, the sole source being the a n t h r a c e n e from coal-tar.   The synthesis of alizarin was first effected by G r a e b e and L i e b e r - m a n n, in 1868.   One of the methods employed in practice has already been described in outline (page 230).   The other commercial process, devised by W. H. P e r k i n, consists in converting anthracene into d i c h l o r a n t h r a c e n e, $C_{14}H_8Cl_2$, by the action of chlorine, and heating the product with sulphuric acid, whereby a mixture is obtained of the two isomeric a n t h r a - q u i n o n e - d i s u l p h o n i c a c i d s described on page 232, with more or less of the monosulphonic acid.   The subsequent fusion with an alkali and an oxidizing agent, and decomposition of the sodium salts by an acid is the same as that already described.   To obtain pure alizarin, a pure monosulphonic acid (free from the disulphonic acid) must be employed,[2] and hence

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[1] RUBERYTHRIC or RUBIANIC ACID, $C_{26}H_{28}O_{14}$, may be obtained by exhausting fresh madder-root with water, adding neutral lead acetate, filtering, and decomposing the precipitate of lead rubianate by sulphuretted hydrogen.   On evaporating the liquid filtrated from the lead sulphide, rubianic acid is obtained in yellow silky needles.

[2] To obtain pure alizarin, the blue shade of commercial alizarin paste may be

Perkin's process is better adapted for the production of anthra-purpurin and flavopurpurin than true alizarin.

Alizarin may also be prepared by heating phthalic anhydride[1] with catechol, a reaction which indicates its constitution:

$$C_6H_4:(CO.OH)_2 + C_6H_4:(OH_2) = C_6H_4:(CO)_2:C_6H_2(OH)_2 + 2OH_2.$$
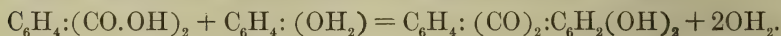
Alizarin crystallizes from alcohol in reddish-yellow prisms or needles containing 3 *aqua*, which it loses at 100°. It melts at 289°–299° C.[2] and sublimes at a somewhat higher temperature in magnificent orange-red needles.

Alizarin is nearly insoluble in cold water, and requires 3220 parts of boiling water for solution. Cold alcohol dissolves it but sparingly, but in boiling alcohol, glacial acetic acid, and glycerin it is more soluble. It is also readily soluble in ether, carbon disulphide, and benzene, and may be extracted by agitation with these solvents. In strong sulphuric acid, alizarin dissolves with dark brownish-red color, and is precipitated unchanged on diluting the solution with water.

In solutions of alum and aluminium sulphate alizarin is almost insoluble, a character which distinguishes it from purpurin, which dissolves in boiling alum solution, forming a yellowish-red and strongly fluorescent liquid.

Alizarin has the characters of a weak acid. It dissolves in solutions of carbonates of the alkali-metals, apparently without decomposing them, and it also dissolves in a boiling solution of sodium acetate, separating again unchanged on cooling; but if the boiling be continued for some time, acetic acid is given off and sodium alizarate remains in permanent solution. With caustic alkalies it reacts to form true compounds or *alizarates*, the solutions of which are violet by transmitted, and purple by reflected, light. A solution of sodium alizarate gives insoluble, colored precipitates or "lakes" with most metallic solutions. Thus with barium and calcium salts it yields purple precipitates (distinction from mono-

dissolved in dilute caustic soda, and the filtered solution treated with barium chloride and heated to boiling. Barium alizarate separates as a precipitate, which is filtered off, washed, and decomposed by hydrochloric acid. The free alizarin is well washed, and can be further purified by sublimation or crystallization from glacial acetic acid.

[1] Alizarin has also been synthesized from hemipic acid, which is dimethoxyphthalic acid (K. Lagodzinski, *Ber.*, xxviii, p. 1427).

[2] This is the melting point of alizarin according to Claus and Wildgerodt. Schunck gives 282° as the melting point.

hydroxyanthraquinone) which are soluble in water containing carbonic acid. With aluminium and tin alizarin forms red lakes, and has such affinity for these metals that it is capable of decomposing dilute solutions of nitrates or chlorides containing them. With ferric salts, sodium alizarate yields a black-violet precipitate, but with ferrous salts a violet precipitate is formed. An alcoholic solution of free alizarin also gives a purple precipitate with ferric chloride.

By heating in the solid state with zinc-dust, alizarin is reduced to a n t h r a c e n e, $C_{14}H_{10}$. If dissolved in weak soda and treated in the cold with zinc-dust, the violet solution becomes red. When alizarin is boiled with zinc-dust and ammonia it is reduced to a body of the formula $C_{14}H_{10}O_3$, to which the name a n t h r a - r o b i n has been given.[1]

The solution of alizarin in ammonia or carbonated alkali differs from that of purpurin in being non-fluorescent, but exhibits a characteristic absorption-spectrum, having a well-defined band in the yellow, and another narrower one between the orange and red. There is also another faint band about E, scarcely distinguishable from the general absorption occurring in that region. The absorption spectra of the solutions of alizarin in ether and carbon disulphide are not characteristic.

When boiled with acetic anhydride, alizarin yields a m o n o - a c e t y l - d e r i v a t i v e, and on prolonged boiling d i a c e t y l - a l i z a r i n, $C_{14}H_6(O.C_2H_3)_2O_2$.

ALIZARIN-SULPHONIC ACID. $C_{14}H_5O_2(OH)_2(SO_3H)$. This body is formed by heating alizarin with fuming sulphuric acid until the product is completely soluble in water. The liquid is then

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[1] ANTHRAROBIN has been recommended in skin-diseases as a substitute for chrysarobin or chrysophanic acid (page 234), as it is said to be less liable to produce inflammation of the cuticle. It is prepared by boiling commercial alizarin with zinc-dust and dilute ammonia, filtering the ammoniacal solution into hydrochloric acid, and collecting, washing, and drying the precipitate. The similar product from purpurin is called *anthrarobin P* or *T*.

Commercial anthrarobin is a yellowish-white powder, permanent in the air, and insoluble in water and dilute acids, but readily soluble with brownish-yellow color in dilute solution of alkalies and alkaline earths, the solutions by contact with air or oxygen changing to green and blue, and finally to violet.

Anthrarobin dissolves with difficulty in benzene or chloroform, but is soluble with moderate facility in cold, and very easily in boiling alcohol. The alcoholic solution may be mixed with glycerin without precipitation.

Commercial anthrarobin contains a trace of zinc, but the entire ash should not exceed 0.3 per cent.

diluted, and the unaltered sulphuric acid precipitated by lime or baryta.

Alizarin-sulphonic acid is freely soluble in water, and forms three series of salts, according to the number of hydrogen atoms replaced. The salts of the alkali-metals containing one atom of base are yellow or orange, and soluble in water; those with two atoms are reddish-violet; and those with three atoms intensely violet.

Sodium Alizarin-sulphonate, $C_{14}H_5O_2(OH)_2(SO_3Na)$, constitutes the coloring matter known in commerce as *alizarin carmine*, *alizarin powder W*, and *alizarin WS* or *WSI*. It forms an orange-yellow powder, easily soluble in water or alcohol with orange or brownish-yellow color. The solution is turned bright yellow by hydrochloric acid and violet by caustic soda. In strong sulphuric acid the dye dissolves with yellowish-red color, changing to bright yellow on dilution. Alizarin carmine dyes wool mordanted with alumina scarlet, while tin mordants give orange and chromium claret-red shades; but the colors are not so bright as those obtained with sulphonated azo-dyes.

BETA-NITROALIZARIN. $C_6H_4:C_2O_2:C_6H(NO_2)(OH)_2$.   By direct treatment with nitric acid, alizarin is converted into p h t h a l i c   a c i d, $C_6H_4(COOH)$ (page 236); but by the action of nitric acid on alizarin dissolved in glacial acetic acid or petroleum spirit, b e t a - n i t r o - a l i z a r i n is obtained. This body, which constitutes the *alizarin orange* of commerce, was formerly prepared by exposing cloth dyed with alizarin red to nitrous fumes, but is now directly obtained by treating alizarin in nitrobenzene solution with nitric acid of 30°–40° Baumé. When pure, nitro-alizarin forms yellow needles or leaflets, which melt at 244° C. and sublime at a higher temperature with partial decomposition. It is nearly insoluble in water, but dissolves in glacial acetic acid. The solution in caustic soda is magenta-red, and on treatment with zinc-dust gradually becomes blue and then yellowish-brown, the indigo-blue color re-turning on exposing the filtered liquid to the air. Other reactions of alizarin orange are given in the tables.

β-nitro-alizarin derives its chief practical interest from its reaction with glycerol and sulphuric acid,[1] whereby it is converted

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[1] One part of nitro-alizarin in fine powder is heated with five parts of strong sulphuric acid and five of absolute glycerin to 150° C. When the reaction is completed, the product is boiled with excess of water, when the coloring matter dissolves, but is deposited on cooling as a flocculent brown precipitate. When this is washed with water, it loses sulphuric acid and becomes blue.

into d i h y d r o x y a n t h r a q u i n o n e - q u i n o l i n e, or *alizarin blue*, according to the following equation:

$$C_6H_4: C_2O_2: C_6 \begin{cases} (a1)OH \\ (\beta1)OH \\ (\beta2)H \\ (a2)NO_2 \end{cases} + \begin{matrix} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{matrix} =$$

$$C_6H_4: C_2O_2: C_6 \begin{cases} OH \\ OH \\ CH:CH. \\ N \ : CH. \end{cases} + O_2 + 3OH_2.$$
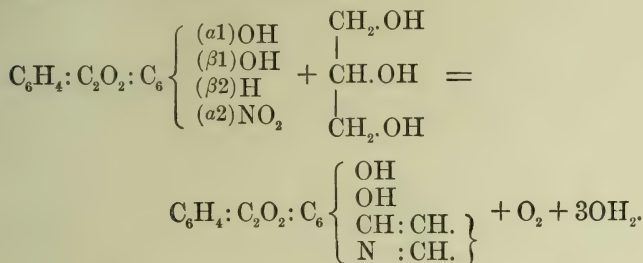
Alizarin Blue, $C_{17}H_9NO_4$, has the constitutional formula shown above. In the pure state it forms dark blue or brownish-violet needles, which melt at 270°, and may be partially sublimed without decomposition. In commerce, alizarin blue occurs as minute shining crystals, or as a dark violet paste containing 10 per cent. of the dry substance. The pure coloring matter can be obtained by boiling the dried paste with glacial acetic acid, the alizarin blue being deposited in crystals on cooling. It is insoluble in water, but dissolves with blue color in hot alcohol, and is sparingly soluble in benzene.

Alizarin blue exhibits both acid and basic characters, a property doubtless due to the simultaneous presence of OH groups and a pyridine residue in the molecule. With dilute sulphuric acid alizarin blue unites to form a brown compound, which is decomposed by washing with water. In strong sulphuric acid it dissolves with red, and in phosphoric and arsenic acids with reddish-yellow color.

In dilute caustic alkalies alizarin blue dissolves with greenish-blue color, but the solution is precipitated by excess of alkali. By treating the solution of alizarin blue in caustic alkali with metallic solutions a series of insoluble lakes may be obtained. The compounds with lime, baryta, and ferric oxide are greenish-blue, that with nickel oxide blue, and those with alumina and oxide of chromium bluish-violet.

When treated with zinc-dust in alkaline solution, alizarin blue is reduced with red coloration, but the blue color returns on exposing the filtered liquid to the air. Other reducing agents may be employed, and the property may be applied for the production of an alizarin blue vat, similar to that used in indigo-dyeing. Alizarin blue is too expensive to be used generally as a substitute

for indigo, and its tendency to form insoluble lakes is not in its favor. The color is not so fast to light as indigo, but is less readily attacked by oxidizing agents, such as hypochlorites, chromic acid, and alkaline solutions of ferricyanides.

The inconvenience attending the employment of ordinary alizarin blue can be overcome by converting it into a soluble form, by treating the commercial paste with a concentrated solution of acid sodium sulphite. After standing ten days or a fortnight, the liquid is filtered, and the new coloring matter obtained in the solid state by evaporation at a low temperature or salting out.

Alizarin Blue S, or *Soluble Alizarin Blue,* obtained as above described, is the sodium bisulphite compound of dihydroxyanthraquinone-quinoline. It occurs in commerce as a dark purple or chocolate-brown powder, which dissolves easily in water with yellowish-brown color. In strong sulphuric acid the solid dye dissolves with deep yellow color, and on dilution with water the liquid yields a brownish precipitate. Dilute hydrochloric acid changes the color of the aqueous solution to reddish-yellow, and soda turns it to bluish-violet. With excess of a strong acid or alkali, the bisulphite compound is decomposed with precipitation of the blue; but the solution is unaffected by salts of calcium, magnesium, or chromium, or by acetic or tartaric acid. On heating the aqueous solution above 70° C., the bisulphite compound is decomposed, and the insoluble blue coloring matter is precipitated. This reaction is extensively applied in practice, and the color produced being less affected by light than that given by insoluble alizarin blue, the soluble variety has almost superseded the older coloring matter both in printing and dyeing.

Soluble alizarin blue is now a formidable rival of indigo in wool-dyeing. The wool is first mordanted by sulphuric acid and bichromate of potassium, and is then immersed in a bath of alizarin blue S, to which sufficient acetic acid has been added to neutralize any earthy carbonates existing in the water. The colors thus obtained are said to be as fast as indigo to light and milling.[1]

On the fibre, alizarin blue is unchanged by soap, soda, or solution of bleaching powder. When dyed on wool with a chrome mordant, nitric acid produces an orange color, but otherwise the color is discharged. Dilute hydrochloric solution turns the color

[1] Alizarin blue is now being tried on a large scale in the Prussian army, the English navy, and on the Atlantic liners.

to violet, and soda to bluish-green, while an acid solution of stannous chloride changes the color to a brownish-yellow. When treated with phosphoric acid of 1.435 sp. gravity, alizarin blue is dissolved from the fibre with orange color, and the solution, after dilution with water, is turned blue on adding ammonia. The absorption-spectrum of alizarin blue is characteristic, and the fact may be utilized for its detection.

Trihydroxyanthraquinones. $C_{14}H_5O_2(OH)_3$.

Of the five known bodies of this constitution (formulated on page 234) four have a practical interest as coloring matters, and are described below. Of h y d r o x y c h r y s a z i n, the fifth discovered isomer, very little is known.

ANTHRAGALLOL. $C_6H_4: C_2O_2: C_6H(OH)_3$. [OH: OH: OH $= a1$:-$\beta1: \beta2$]. This body has not yet been obtained from anthracene. It is prepared by the action of phthalic anhydride on pyrogallol in presence of sulphuric acid or chloride of zinc:—

$$C_6H_4: C_2O_2: O + C_6H_3(OH)_3 = C_6H_4: C_2O_2: C_6H(OH)_3 + H_2O.$$
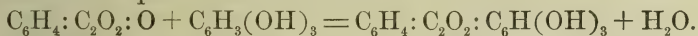
It may also be obtained by acting with gallic acid on benzoic acid in presence of sulphuric acid:—

$$C_6H_5.CO.OH + C_6H_2(OH)_3.CO.OH = C_6H_4: C_2O_2: C_6H(OH)_3 + 2H_2O.$$
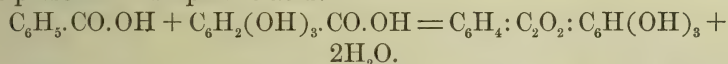
Anthragallol forms the essential constituent of the coloring matter known as *anthracene brown*. It occurs as a dark brown paste, insoluble in water, but dissolving in alcohol with yellow color.

PURPURIN. $C_6H_4: C_2O_2: C_6H(OH)_3$ [OH: OH: OH $= a1: \beta1: a2$]. Purpurin occurs to a considerable amount in old madder-root, mixed with alizarin, from which it may be separated by treating the mixture with a boiling solution of alum, in which alizarin is insoluble. Purpurin may also be prepared artificially by oxidizing alizarin or quinizarin with manganese dioxide and sulphuric acid. A preferable plan is to dissolve alizarin in strong sulphuric acid, heat the liquid to 150°–160° C., and gradually add dry arsenic acid. When the reaction is over, the liquid is diluted with water and the precipitate separated and treated with a hot concentrated solution of alum, the liquid is filtered from the residue of unchanged alizarin, and the purpurin precipitated from the filtrate by adding hydrochloric acid.[1] The product may be purified by crystallization from alcohol.

[1] The proportion of purpurin present in the commercial paste may be similarly

Purpurin crystallizes from its solution in hot spirit in yellowish-red needles or prisms, containing $C_{14}H_5(OH)_3O_2 + H_2O$. It begins to sublime at 150° and melts at 153°, but is more readily decomposed by heat than is alizarin. In water, purpurin is more soluble than alizarin, and the solution in hot water free from alkali has a yellow color. Purpurin also dissolves in alcohol and ether.

In caustic alkalies, purpurin dissolves easily with a magenta or purple-red color. It forms a compound with soda, which crystallizes in well-defined long prisms. The alkaline solutions of purpurin become decolorized on prolonged exposure to light. On strongly acidulating a solution of purpurin in an alkali with hydrochloric acid, p u r p u r i n h y d r a t e is thrown down. The artificial purpurin paste probably consists chiefly of this body. When heated, it loses its water of hydration, and changes into ordinary purpurin. In warm alcohol it dissolves more readily than ordinary purpurin.

When heated with aqueous ammonia under pressure, purpurin is converted into p u r p u r i n a m i d e, $C_{14}H_5(NH_2)(OH)_2O_2$. Owing to the formation of this body, an ammoniacal solution of purpurin, if kept for several weeks, loses its power of dyeing mordanted cloth. On neutralizing the solution, the purpurinamide forms a dark crystalline precipitate, soluble in alcohol or a large quantity of hot water, but separating again on cooling in long crimson needles, which exhibit a deep green metallic reflection. It dissolves freely in fuming nitric acid (sp. gr. 1.5) at the temperature of boiling water, and on cooling the solution deposits magnificent scarlet crystals, which are insoluble in water, ether, and carbon disulphide, and only slightly soluble in alcohol.

With acetic anhydride, purpurin forms a t r i a c e t y l d e r i-v a t i v e of the composition $C_{14}H_5(OC_2H_3O)_3O_2$, which crystallizes in yellowish needles fusing at 190°–193° C. An alcoholic solution of purpurin gives with alcoholic lead acetate a dark crimson precipitate, which dissolves on treatment with an excess of the reagent. to form a fine crimson solution, the spectrum of which shows three absorption-bands. Alizarin when similarly treated gives a purple coloration or precipitate.

An alcoholic solution of purpurin gives with alcoholic copper

determined by boiling the sample with a strong solution of alum or aluminium sulphate, filtering, precipitating the filtrate by hydrochloric acid and weighing the dried precipitate.

acetate a dark reddish-yellow precipitate, whereas alizarin, if pure, gives a purple solution, but no precipitate, when treated similarly.

With lime and baryta water purpurin yields purple-red precipitates, and dyes cloth mordanted with alumina a color varying from scarlet to dark red, without any shade of blue. Purpurin dyes cotton mordanted with ferric salts purple or black.

The most characteristic reaction of purpurin is its property of dissolving in a hot solution of alum with reddish-yellow color and greenish-yellow fluorescence. The purpurin-alumina lake behaves similarly. The fluorescence is seen to perfection in a liquid prepared by adding a solution of purpurin in sodium carbonate to one of alum which has been previously treated with tartaric acid and sodium carbonate in quantity sufficient to prevent precipitation.

The absorption-spectrum of purpurin is characteristic. A solution of purpurin in alum or alkaline carbonate, if of suitable strength, gives two well-defined absorption-bands in the green, the less refrangible—situated about twice as far from line D as from line E[1]—being particularly sharp and black.[2] The absorption-spectrum of the solution of purpurin in carbon disulphide contains four nearly equidistant absorption-bands, of which the first, which is somewhat more refrangible than the D line, is the narrowest, the second and third broader, but very distinct, while the fourth is scarcely distinguishable from the general absorption. An ethereal solution of purpurin is faintly fluorescent, and shows a very dark narrow absorption-band slightly more refrangible than E, and a second wider and less defined band at F.

The detection of alizarin by a similar method is far less delicate, since alum cannot be used to separate it from the accompanying impurities, some of which produce absorption in that part of the spectrum in which all but the least refrangible of the absorption-bands occur, and this band is not the most intense or characteristic of those produced by alizarin (S t o k e s, *Jour. Chem. Soc.*, xii. 219).

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[1] According to H. M o r t o n, the refrangibility of the absorption-bands of a solution of purpurin in alum is sensibly affected by the temperature of the solution and the proportion of alum contained in it.

[2] By boiling a very small quantity of the root with alum, and observing the absorption-spectrum and fluorescence of the filtered liquid, Stokes detected purpurin in upwards of twenty species of the family *Rubiaceæ*, comprising the genera *Rubia*, *Asperula*, *Gallium*, *Crucianella*, and *Scherardia*.

To detect small quantities of alizarin in purpurin, a solution of the coloring matter in caustic soda should be exposed to the light till all the purpurin is destroyed. The liquid is then treated with dilute sulphuric acid and agitated with ether, alizarin being subsequently sought for in the evaporated ethereal solution.
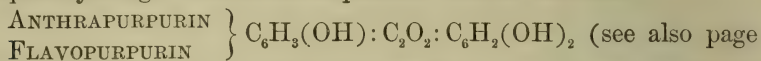
ANTHRAPURPURIN $\Big\}$ $C_6H_3(OH):C_2O_2:C_6H_2(OH)_2$ (see also page
FLAVOPURPURIN
232). These two isomeric bodies differ from each other and from purpurin simply in the position occupied in the molecule by the hydroxyl groups. They are produced by fusing *beta*-anthraquinone-disulphonic acid and *alpha*-anthraquinone-disulphonic acid, respectively, with caustic soda and potassium chlorate (page 232). Both are valuable coloring matters, and exist in various brands of commercial alizarin. Anthrapurpurin is as important a coloring matter as alizarin itself, and used with it increases its brilliancy, while alone it gives very brilliant scarlet shades. *Alizarin for reds* consist chiefly of anthrapurpurin, while flavopurpurin gives yellower shades. Both coloring matters present a close resemblance to alizarin, and the general reactions of the commercial pastes are shown in the tables. In the following table, the principal distinctions between anthra- and flavo-purpurin are exhibited:

	ANTHRAPURPURIN.	FLAVOPURPURIN.
Positions of the OH groups.	$\beta'1 : a1 : \beta1$.	$\beta'2 : a1 : \beta1$.
Appearance.	Orange needles; anhydrous.	Golden - yellow needles; anhydrous.
Solubility in alcohol.	Easily soluble in boiling alcohol.	Easily soluble even in cold alcohol.
Solubility in hot benzene.	Almost insoluble.	Soluble.
Solubility in boiling water.	Slight; solution turns red on prolonged boiling.	Slight; solution remains yellow after prolonged boiling.
Solubility in solution of alum.	Slightly soluble with orange color on boiling; separates again on cooling.	Insoluble.
Color of solution in strong sulphuric acid.	Dull violet color, changing to fine red-violet on adding a trace of sodium nitrite.	Red-brown.
Color of solution in caustic alkali.	Violet (but redder than an alkaline solution of alizarin); two absorption-bands simulating those of alizarin.	Purple (redder shade than with anthrapurpurin); on dilution, pure red. Two absorption - bands, more refrangible than those of alizarin, and a characteristic broad band in the blue.
Color of solution in ammonia.	Violet; no absorption-bands.	Yellowish-red; no absorption-bands.
Color of solution in sodium carbonate.	Violet.	Yellowish-red.
Reaction with alcoholic solution of lead acetate.	Purple precipitate, dissolving with violet color on boiling with excess of the reagent.	Reddish - brown precipitate, dissolving very sparingly on boiling with excess of the reagent, with red color.
Reaction with alcoholic solution of cupric acetate.	Fine violet color.	Red coloration.

Anthrapurpurin and flavopurpurin are now met with in commerce in a state of almost perfect purity, but sometimes are very impure. G. Jellinek (*Ber.*, xxi. 2524; *J. S. C. Ind.*, vii. 743) states that the article supplied as pure flavopurpurin by various

German alizarin makers sometimes contains as much as 30 per cent. of non-tinctorial substances, chiefly anthraflavic acid. For the detection of these impurities in commercial flavopurpurin, Jellinek recommends that the sample should be dissolved in alkali, and the solution treated with lead acetate. The precipitate is well washed with hot water, and decomposed by sulphuric acid in presence of alcohol. The coloring matter is then obtained from the alcoholic solution by fractional crystallization.

The following table exhibits the characteristic differences between alizarin and the three purpurins:—

NAME.	WITH NaOH.	WITH H_2SO_4.	SUBLIMATION POINT.
Alizarin	Blue-violet.	Brown-red.	Below 160° C.
Anthrapurpurin . . .	Violet.	Brown.	At 160° C.
Flavopurpurin . .	Purplish-red.	Red-violet.	170° C.
Purpurin	Red.	Cherry-red.	150° C.

Fibres dyed with alizarin or flavopurpurin lakes or with the aluminium lake of anthrapurpurin are not changed in an alkaline solution of potassium ferri-cyanide, whereas the color on fibres dyed with anthrapurpurin on an iron mordant, or with purpurin are destroyed.

Commercial Alizarin. Alizarin Paste.

Commercial alizarin always occurs in the form of an ochre-yellow or brownish-yellow paste,[1] consisting of the solid coloring matters in a hydrated state mixed with a definite proportion of water.

Alizarin paste ordinarily contains 20 per cent. of solid matter. The strength is easily ascertained by drying a fair sample at 100° C. By exposure to this temperature the alizarin is rendered anhydrous, loses the slight solubility it previously possessed, and becomes wholly unfit for dyeing.[2] The *residue*, after drying, should be yellow—not dark brown. After weighing, the residue should be ignited at a dull red heat. The *ash* obtained should not

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[1] Dry alizarin may be prepared by mixing the paste with starch and pressing and drying.

[2] The same statement applies to alizarin paste which has been frozen, and hence it is customary during severe weather to protect the coloring matter from the cold.

exceed 1 per cent. of the weight of the dried residue, and should be practically free from *iron*.[1]

According to B e n e d i k t and K n e c h t, commercial alizarin is liable to contain glycerin, turkey-red oil, and other thickening agents, for the detection of which they recommend dilution of the paste with water and filtration of the liquid, when a perfectly colorless filtrate should be obtained, which may contain small quantities of sodium chloride and other salts, but should leave no syrupy residue of glycerin on cautious evaporation. A practical objection to this method of examination exists in the great difficulty, sometimes amounting to impossibility, which attends the filtration of alizarin paste diluted with water. If the presence of glycerin or turkey-red oil be suspected, it would probably be preferable to examine the residue left on evaporating the paste to dryness at 100°.

Besides true alizarin, the commercial paste contains more or less of the dihydroxy-anthraquinones isomeric with alizarin, as well as several of the mono- and tri-hydroxyanthraquinones. All these bodies present a very close general resemblance to alizarin proper, but all except the trihydroxyanthraquinones (flavopurprin and anthrapurpurin) are valueless as dyes, and these latter give very different shades from those produced by pure alizarin.

The following method is given by B e n e d i k t and K n e c h t for recognizing the constituents of commercial alizarin paste:—A small quantity of the sample is dissolved in a solution of sodium carbonate, and the liquid filtered. The r e s i d u e consists of *anthraquinone* and *monohydroxyanthraquinone*, which may be separated by means of dilute caustic soda solution, in which only the latter is soluble. The filtered carbonate of sodium s o l u t i o n is acidulated with hydrochloric acid, and the p r e c i p i t a t e boiled with milk of lime, which will dissolve any *anthraflavic* and *isoanthraflavic acids* with red color.[2] On filtering and acidulating the

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[1] The so-called "soluble alizarin" consists of sodium boro-alizarate. It is prepared by dissolving one part of alizarin and two parts of borax in boiling water, and evaporating the solution to dryness. It is said that a solution of soluble alizarin in distilled water gives a very delicate test for the presence of lime in water, a flocculent precipitate being formed with the merest trace of calcium salt.

[2] Both these bodies, as also monohydroxyanthraquinone, are valueless as dyes. Their presence in commercial alizarin may be detected by boiling the sample with milk of lime and filtering, when a yellow or brownish-red solution will be

f i l t r a t e these impurities will be reprecipitated, and may be
collected, washed, and weighed. The insoluble l i m e - l a k e is
removed from the filter and decomposed by agitation with dilute
hydrochloric acid, and the separated coloring matter washed and
weighed, or dissolved in ether and recovered by evaporating the
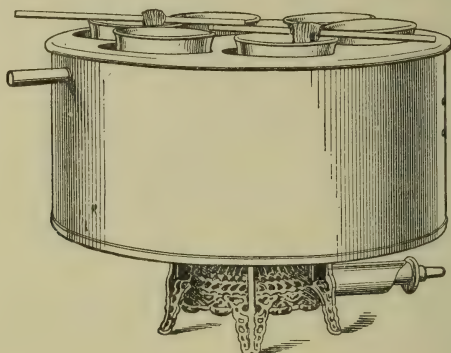
Figure 2.

ethereal solution. The residue thus obtained will contain the
alizarin of the sample, mixed with an anthrapurpurin or flavo-
purpurin which may be present. According to S c h u n k and
R ö m e r, the detection and approximate determination of these

obtained. The following are the chief differences between these three allied
substances :—

	β-MONOHYDROXY-ANTHRAQUINONE.	ANTHRAFLAVIC ACID.	ISOANTHRAFLAVIC ACID.
Action of heat.	Sublimes, without melting, above 285°.	Melts above 330°, and sublimes.	Melts above 300°, and sublimes.
Action of water.	Easily soluble; insoluble in acidulated water.	Insoluble.	Insoluble.
Action of aqueous alcohol.	Separates from hot solution in yellow laminæ or needles.	Separates from solution in long, anhydrous. yellow needles or laminæ.	Separates from solution in hydrated crystals.
Action of hot, strong, sulphuric acid.	. . .	Forms yellow solution.	Forms deep red solution.
Action of cold baryta water.	Soluble with reddish-yellow color.	Insoluble.	Easily soluble with dark red color.
Action of hot lime water.	Soluble with reddish-yellow color.	Slightly soluble, cold; nearly insoluble, hot; solution yellowish-red.	Easily soluble with dark red color.

three bodies in admixture can readily be effected as follows: The mixture is dried at 100° C., and then placed between two glass plates, separated from each other by a leaden ring some millimetres in thickness. The whole is heated in an air-bath to 130°–150°, at which temperature the *alizarin* alone sublimes. On raising the temperature to 170°, a crystalline sublimate of mixed *flavopurpurin* and *anthrapurpurin* is obtained, the former of which assumes the shape of fine reddish-yellow needles, while the latter sublimes in compact, well-defined rhombic crystals. A separation of the two isomers may be effected by boiling with benzene, in which only flavopurpurin dissolves.[1]

[1] For the analysis of alizarin pastes as obtained from filter presses, the percentage of *moisture* is determined by evaporating a weighed sample in a flat platinum dish at 100°. After weighing, the *inorganic matter* present is determined by incineration. Usually the ash, which should not exceed 0.2 per cent. in a 20 per cent. paste, consists of either sodium or calcium salts but sometimes lead and iron are also present, though contamination of alizarin with iron should be carefully avoided if in dyeing bright shades are required. The *tinctorial properties* of the paste are then compared with those yielded by a standard sample of known strength and shade. In this operation a special five-striped cotton cloth is best employed, the mordants on which consist of strong and weak aluminium and iron salts and a mixture of the two respectively. Of this, 10-in. lengths are most suitable. The dye vessels, preferably of glass or porcelain, and of about 600 c.c. capacity, are arranged in rows in a suitable copper water-bath heated with gas (see figure 2). Five grms. of the 20 per cent. paste under examination is suspended in a litre of water and 50–70 c.c. of this, together with 4 c.c. of a 1 per cent. solution of calcium acetate are added to 500 c.c. of water in the dye vessel. The temperature is gradually raised to 80° during one hour, the heat being maintained at that temperature for half an hour. After washing in cold water, the fents are well beaten with a wooden mallet and again rinsed, the treatment being continued until the loosely-adhering particles of alizarin are almost entirely removed. This is followed by two soaping operations, each lasting one hour, the first at 60° and the second at 80°, conducted in a large tinned copper vessel, which contains for each fent a solution of 0.5 grm. of curd soap in a litre of water. The patterns after washing are dried at the ordinary temperature. Swatches of turkey-red cloth are very frequently dyed, and these, after the ordinary soaping, are heated under pressure with soap solution, to which a trace of stannous chloride has been added to give them a more brilliant appearance.

m-hydroxyanthraquinone may be detected by treating a hot alkaline solution with baryta water and filtering the precipitate. A red colored filtrate is obtained which on acidification deposits a yellow precipitate.

Anthra- and iso-anthraflavic acids. To a sample of the paste suspended in boiling water barium hydrate is added and the barium lake filtered off. A red colored filtrate giving a yellow precipitate on neutralization indicates the presence of these substances.—P e r k i n (*Jour. Soc. Dyer's*, etc., 1897, 81).

COMMERCIAL NAME.	FORMULA.	REMARKS.
Alizarin Yellow C.	$C_6H_2 \begin{cases} (1)OH \\ (2)OH \\ (3)OH \\ (4)CO.CH_3 \end{cases}$	From Pyrogallol.
Alizarin Yellow A.	$C_6H_5(1)CO(1)C_6H_2 \begin{cases} (2)OH \\ (3)OH \\ (4)OH \end{cases}$	From Pyrogallol.
Alizarin V, VI, P, No. 1, Ie. Alizarin for violet.	$C_6H_4 \begin{Bmatrix} (2)CO(2) \\ (3)CO(3) \end{Bmatrix} C_6H_2 \begin{cases} (1)OH \\ (6)OH \end{cases}$	From anthraquinone-monosulphonic acid.
Alizarin RG, GI, SDG, X, No. 10, CA. Flavopurpurin.	$C_6H_3 \begin{Bmatrix} (2)CO(2) \\ (5)OH \\ (3)CO(3) \end{Bmatrix} C_6H_2 \begin{cases} (1)OH \\ (6)OH \end{cases}$	From a-anthraquinone-disulphonic acid.
Alizarin SC, SX, GD, RX, SC, SX extra, RF. Anthrapurpurin.	$C_6H_3 \begin{Bmatrix} (2)CO(2) \\ (6)OH \\ (3)CO(3) \end{Bmatrix} C_6H_2 \begin{cases} (1)OH \\ (6)OH \end{cases}$	From β-anthraquinone-disulphonic acid.
Alizarin No. 6. Purpurin.	$C_6H_4 \begin{Bmatrix} (2)CO(2) \\ (3)CO(3) \end{Bmatrix} C_6H \begin{cases} (1)OH \\ (4)OH \\ (6)OH \end{cases}$	From alizarin by oxidation.
Alizarin Orange A, OR, OG, N, AO, AOP.	$C_6H_4 \begin{Bmatrix} (2)CO(2) \\ (3)CO(3) \end{Bmatrix} C_6H \begin{cases} (1)OH \\ (5)NO_2 \\ (6)OH \end{cases}$	From nitrated alizarin.
Anthracene Brown R, G. Alizarin Brown. Anthrogallol.	$C_6H_4 \begin{Bmatrix} (2)CO(2) \\ (3)CO(3) \end{Bmatrix} C_6H \begin{cases} (1)OH \\ (5)OH \\ (6)OH \end{cases}$	From gallic acid.
Galloflavin.	$C_{13}H_6O_9$ (constitution not known).	From gallic acid.
Alizarin Black S, SW. Alizarin Blue-Black SW. Naphthazarin S.	$C_{10}H_4 \begin{cases} (1)O \\ (4)O \\ (7)OH \\ (8)OH \end{cases} +NaHSO_3$	From dinitronaphthalene.
Alizarin Blue. Alizarin Blue R, GW, A, DNW, F, R, RR, AB.	$C_6H_4 \begin{Bmatrix} (2)CO(2) \\ (3)CO(3) \end{Bmatrix} C_6 \begin{cases} (1)OH \\ (6)OH \\ (4)CH=CH \\ (5)N = CH \end{cases}$	From β-nitroalizarin.
Alizarin Yellow.	$C_{14}H_{10}O_{10}$	From ellagic acid.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Yellow paste; yellow solution.	Brown.	. .	Yellow.	. .	Soluble in alcohol.
Yellow paste; yellow solution.	Deeper yellow.	No change.	Yellow.	White ppt.	. . .
Yellow paste; insoluble in cold water; slightly soluble in hot water.	Violet.	No change.	Orange.	Orange ppt.	On cotton mordanted: Al—red. Fe—violet. Cr—brown.
Yellow paste; slightly soluble in boiling water.	Violet.	. .	Brown.	Orange ppt.	Al—red. Soluble in alcohol. With ammonia brown solution.
Yellow paste; slightly soluble in boiling water.	Violet.	. .	Red.	Orange ppt.	Al—red. With ammonia violet solution.
Brown paste; slightly soluble in hot water.	Magenta-red.	. .	Orange.	Brown ppt.	Soluble in alcohol. Al—red. Fe—purple. Cr—brown.
Brown paste; insoluble in hot or cold water.	Magenta-red solution.	. .	Yellow.	Yellow ppt.	Soluble in acetic acid. Al—orange. Fe—red-violet. Cr—red-brown.
Brown paste; insoluble in water.	Greenish-blue solution.	No change.	Brown.	Brown ppt.	Soluble in alcohol. Cr—brown.
Yellow paste; insoluble in water.	Yellowish-brown solution.	No change.	Orange.	Gray ppt.	Cr—greenish-yellow. Slightly soluble in boiling alcohol.
Black paste; soluble in hot water.	Blue.	Brownish-red.	Yellow; on heating red, SO$_2$ evolved.	Black ppt.	Soluble in alcohol. Cr—black.
Blue crystals; insoluble in water.	Green in alcohol solution.	Orange in alcohol solution.	Carmine-red.	Orange.	Al—bluish-violet. Fe—greenish-blue. Cr—India-blue. Soluble in alcohol.
Brown paste; insoluble in water.	Brown solution.	. .	Brown.	Ellagic acid ppt.	Slightly soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Anthracene Yellow.	$C_6 \begin{cases} (1)OH \\ (2)O\text{———}CO \\ (3)C(CH_3)=CH \\ (4)Br \\ (5)Br \\ (6)OH \end{cases}$	From Pyrogallol.
Alizarin Bordeaux B, BD, G, GG.	$C_6H_2 \begin{cases} (1)OH \\ (2)CO(2) \\ (3)CO(3) \\ (4)OH \end{cases} C_6H_2 \begin{cases} (1)OH \\ (6)OH \end{cases}$	Oxidation of alizarin.
Alizarin Cyanin R.	$C_6H_2 \begin{cases} (1)OH \\ (2)CO(2) \\ (3)CO(3) \\ (4)OH \end{cases} C_6H \begin{cases} (1)OH \\ (4)OH \\ (6)OH \end{cases}$	Oxidation of alizarin bordeaux.
Alizarin Cyanin G.	.	Treatment of preceding with air and ammonia.
Alizarin Red S. Alizarin Carmine. Alizarin WS, W, SA.	$C_6H_4 \begin{cases} (2)CO(2) \\ (3)CO(3) \end{cases} C_6H \begin{cases} (6)OH \\ (5)OH \\ SO_3Na \end{cases}$	From alizarin with concentrated H_2SO_4.
Alizarin Maroon.	$C_6H_4 \begin{cases} (2)CO(2) \\ (3)CO(3) \end{cases} C_6 \begin{cases} (1)OH \\ (4)OH \\ (5)NH_2 \\ (6)OH \end{cases}$	From nitroalizarin.
Alizarin Blue S. Alizarin Blue Soluble Powder ABS. Anthracene Blue S.	$C_6H_4 \begin{cases} (2)C\begin{cases}OH\\SO_3Na\end{cases}(2) \\ (3)C\begin{cases}OH\\SO_3Na\end{cases}(3) \end{cases} C_6(OH)_2 \begin{matrix} N=CH \\ | \\ CH=CH \end{matrix}$	From alizarin blue.
Alizarin Indigo Blue S.	$\begin{matrix}HO(1)\\HO(4)\\HO(6)\end{matrix} \Big\} C_6 \begin{cases} (2)C\begin{cases}OH\\SO_3Na\end{cases}(2) \\ (3)C\begin{cases}OH\\SO_3Na\end{cases}(3) \end{cases} C_6(OH)_2 \begin{matrix} N=CH \\ | \\ CH=CH \end{matrix}$	From alizarin green.
Alizarin Green S.	$\begin{matrix}HO(1)\\HO(4)\end{matrix} \Big\} C_6H_2 \begin{cases} (2)C\begin{cases}OH\\SO_3Na\end{cases}(2) \\ (3)C\begin{cases}OH\\SO_3Na\end{cases}(3) \end{cases} C_6(OH)_2 \begin{matrix} N=CH \\ | \\ CH=CH \end{matrix}$	From alizarin blue.
Rufigallol.	$\begin{matrix}HO(1)\\HO(4)\\HO(5)\end{matrix} \Big\} C_6H \begin{cases} (2)CO(2) \\ (3)CO(3) \end{cases} C_6H \begin{cases} (1)OH \\ (5)OH \\ (6)OH \end{cases}$	From gallic acid.
Fast Black B.	Not determined.	From dinitronaphthalin.
Fast Black BS.	Not determined.	From fast black B.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
White paste; slightly soluble in water.	Brown solution repp. by acids.	. .	Brown.	. .	. . .
Red paste; insoluble.	Violet solution.	. .	Violet.	Red ppt.	Al—bordeaux. Cr—violet-blue.
Brown paste; insoluble.	Blue solution.	. .	Blue solution.	. .	Al—violet. Cr—blue.
Black paste; insoluble.	Greenish-blue solution.	. . .	Red.	. .	Soluble in alcohol. Al—blue. Cr—bluish-green.
Orange powder; orange solution.	Violet.	Yellow.	Orange.	Yellow.	Soluble in alcohol. Al—scarlet. Cr—bordeaux.
Violet paste; insoluble.	Violet solution.	No change.	Red.	. .	Al—garnet.
Brown powder; brown solution.	Violet.	Orange.	Yellow.	Brown ppt.	Cr—blue.
Dark brown paste; red solution.	Blue.	Blue ppt. on boiling.	. .	. .	Cr—indigo-blue.
Dark brown paste; soluble in cold water.	Violet.	. .	. .	. .	Cr—bluish-green.
Red powder; insoluble in water.	Blue solution.	No change.	Red.	. .	Cr—brown.
Dark blue paste; insoluble in water.	Violet solution in hot NaOH.	. .	Green.	. .	Direct dye for cotton.
Black paste; violet solution.	. .	. .	Green.	. .	Soluble in alcohol. Dyes cotton in cold bath.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Alizarin Garnet R. Alizarin Cardinal.	$C_6H_4 \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6H \left\{ \begin{matrix} (1)OH \\ (6)OH \\ (4)NH_2 \end{matrix} \right.$	From benzoylaliz-arin.
Alizarin Orange G.	$HO(5)C_6H_3 \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6H \left\{ \begin{matrix} (1)OH \\ (6)OH \\ (5)NH_2 \end{matrix} \right.$	From flavopurpurin.
Alizarin Black P.	$HO(5)C_6H_3 \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6(OH)_2 {\begin{matrix} N = CH \\ \big\vert \\ CH = CH \end{matrix}}$	From amidoflavo-purpurin.
Alizarin Black S.	Not determined.	From alizarin black P.
Anthracene Blue WR.	$\left. \begin{matrix} HO(1) \\ HO(4) \\ HO(6) \end{matrix} \right\} C_6H \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6H \left\{ \begin{matrix} (1)OH \\ (4)OH \\ (5)OH \end{matrix} \right.$	From dinitroanthra-quinone.
Anthracene Blue WG.	Not determined.	From dinitroanthra-quinone.
Anthracene Blue WB.	Not determined.	From dinitroanthra-quinone.
Acid Alizarin Blue BB, GR.	$\left. \begin{matrix} SO_3Na(6) \\ HO(1) \\ HO(4) \\ HO(5) \end{matrix} \right\} C_6 \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6 \left\{ \begin{matrix} (1)OH \\ (4)OH \\ (6)OH \\ (5)SO_3Na \end{matrix} \right.$	$\cdots$
Acid Alizarin Green B, G.	$\left. \begin{matrix} SH(1) \\ HO(4) \\ HO(6) \\ SO_3Na(5) \end{matrix} \right\} C_6 \left\{ \begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix} \right\} C_6 \left\{ \begin{matrix} (4)SH \\ (1)OH \\ (5)OH \\ (6)SO_3Na \end{matrix} \right.$	$\cdots$

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hy. drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Red paste; insoluble in water.	Red solution.	Brown.	Brown.	Red ppt.	Soluble in alcohol. Al—bluish-red.
Orange paste; insoluble in water.	Violet.	Brighter.	Orange.	Orange ppt.	Soluble in alcohol. Al—orange.
Black paste; insoluble in water.	Green.	Brown.	Brown.	Brown ppt.	Soluble in alcohol. Cr—violet-gray.
Dark brown paste ; brown solution.	Violet.	Black ppt.	Brown.	Brown ppt.	Cr—gray.
Brown paste; insoluble.	Blue.	. .	Violet.	. .	Soluble in alcohol. Al—violet.
Dark blue paste; violet solution in hot water.	Green.	. .	Brown.	. .	Al—blue.
Dark blue paste; insoluble in water.	. .	. .	. .	. .	Al—greenish-blue.
Red crystals; red solution.	Violet.	No change.	Violet.	Red.	Acid dye for wool.
Dark red crystals; green solution.	Violet.	Violet.	Blue.	Violet.	Acid dye for wool.

The foregoing table shows the characters of the different varieties of alizarin and analogous coloring matters met with in commerce in the form of paste.

Artificial alizarin does not contain purpurin, but in the natural product from madder more or less purpurin is usually present.

In forming an opinion on the quality of commercial alizarin, the performance of a minature dye-test is very useful, and is best conducted as follows: A piece of white calico, some feet in length and four inches wide, is boiled in water containing a little caustic soda, to remove any stiffening agents. After being thoroughly washed, it is immersed in a solution of aluminium acetate ("red liquor") of known measure and strength, the time of immersion and the temperature being duly noted. The calico is then removed, wrung out, and torn into a number of strips three inches wide, which are hung on a string to drain. 0.5 gramme of each sample of alizarin paste to be tested is then weighed out, and put into a corresponding number of wide-mouthed flasks or wide beakers of similar size arranged in a capacious water-bath.[1] 1 litre of water at 40° C. is then poured into each, and the liquid well agitated to facilitate the solution of the alizarin. A strip of the previously mordanted calico is then immersed in the contents of each vessel, care being taken that it is suspended freely so that all parts are in contact with the liquid. This is best done by attaching it to a thread tied

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[1] A very convenient apparatus for the dyeing of small samples consists in an agate enamelled cup which may be heated directly over a small Fletcher burner.
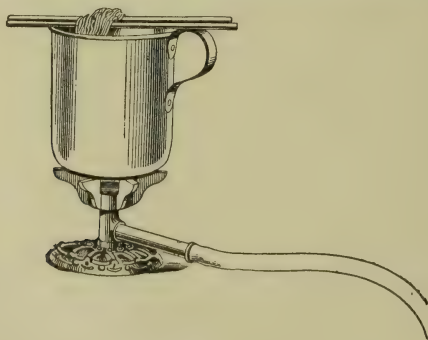
Figure 3.

Either a litre or a half litre cup may be employed. Two stirring rods of glass may be used for the purpose of working the material (either yarn or cloth) in the bath (see figure 3).

to a glass rod placed across the mouth of the flask or beaker. The temperature of the bath is then gradually raised, so that it may reach 75° in about an hour and a half from the immersion of the cloth, after which the temperature is increased to about 90° C. for half an hour longer. The strips of calico are now withdrawn, rinsed in cold water, and dried. Each strip should then be cut into two equal portions, one of which is preserved between the leaves of a book or in other situation away from the light, while others are steeped for half an hour at about 40°–42° C. in one litre of water containing 2 grammes of white curd soap.[1] The strips are then taken out, rinsed in cold water, and put into another bath made with the same quantities of soap and water, with the addition of 0.6 gramme of stannous chloride ("tin crystals"), which is allowed to boil for thirty minutes. The strips are then removed, well rinsed, dried, and preserved in the dark.

Instead of relying on the behavior of the dye-stuff with a single mordant, it is preferable to use a piece of cloth printed in five or six parallel lines with, e. g. (a) strong solution of aluminium acetate; (b) weak aluminium acetate; (c) strong iron acetate; (d) weak iron acetate; (e) mixture of strong solutions of aluminium and iron acetates; (f) mixture of weak solutions of aluminium and iron acetates.[2]

The shades dyed by commercial alizarin depend much on the composition of the coloring matter. Thus the variety giving blue shades (e. g., "alizarin V, or extreme blue shade") consists chiefly of real a l i z a r i n. In dyeing, it yields with alumina mordant a bluish but not very brilliant shade of red; but with a small proportion of mordant very beautiful shades of pink can be obtained. When mordanted with iron, it is used for dyeing and printing fast violets. The yellow shades of commercial alizarin (e. g., alizarin GS) contain a large percentage of a n t h r a p u r-p u r i n and f l a v o p u r p u r i n, and but little real alizarin. Anthrapurpurin yields an almost neutral red with alumina mordants; but flavopurpurin gives a fiery red containing a considerable proportion of yellow, and hence the larger the proportion of flavo-

[1] In some cases, as in the assay of reds, it is desirable to precede the soap treatment by an oil process. This consists of immersing the fabric in a 5 per cent. solution of turkey-red oil, again drying the cloth, and then exposing it to open steam in a suitable box for one hour.

[2] Pieces of cloth printed in the manner recommended, or any other which may be desired, can be obtained by order from many calico-printers.

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purpurin the yellower the shade.   Iron mordants give with anthra-
purpurin and flavopurpurin violets of little or no practical value.
P u r p u r i n does not occur in artificial alizarin, but was a very
common constituent of the dye from madder, which fact was the
chief reason of the different shades produced by natural and arti-
ficial alizarin.

Detection of Alizarin and its Allies on the Fibre.

Alizarin and other allied coloring matters are applied in so
many ways, and with such a variety of mordants, that it is not
possible to describe the method of dyeing shortly.   As the use of a
mordant is essential, they are not so suitable for silk as the sub-
stantive coal-tar dyes.   Alizarin is now used in wool-dyeing, not
merely as a bottoming color for indigo, etc., but as a self-color
with mordants.   Thus when mordanted with alum and tartar it
gives fine reds and scarlets; with stannous chloride, orange shades;
with potassium bichromate, rich claret-browns; with ferrous sul-
phate, shades ranging from bluish-violet to black; with ammonio-.
sulphate of nickel, gray; and with uranium acetate, slate-blue
shades.   These colors are fast to light and air, and resist milling.

The mordants used in dyeing cotton with alizarin are various
compounds of calcium, aluminium, iron, chromium and tin, be-
sides tannic acid and oils.   *Turkey-red*, one of the fastest and most
perfect of the alizarin styles, is dyed by a complicated series of
operations, in which the formation of a compound of alumina with
alizarin and a fatty acid is an essential step.   The method of
operating is substantially that employed in the process of assay
described on page 249.   Treatment with ether changes cloth dyed
turkey-red to a dull cherry-red color, and on evaporating the
ethereal solution a brilliant scarlet fat is left.   This dissolves in
hot caustic soda with purplish-blue color, and on adding hydro-
chloric acid alizarin is precipitated in orange flakes.   *Alizarin violet*
may be obtained in a similar manner to turkey-red, the blue shade
of alizarin being used for its production.   Other violets are ob-
tained by the use of an iron mordant.

Turkey-red is but little affected by a dilute solution of bleaching
powder if free acid be absent, but the other alizarin colors are
gradually bleached.

Alizarin is not affected by potassium bichromate, but free
chromic acid destroys it.   Dilute solutions of permanganate (1 per
cent.) and alkaline solutions of ferricyanides are without effect on

colors produced by artificial alizarin, but *purpurin* is easily oxidized. The last reagent especially is of value for distinguishing colors produced by artificial alizarin from those produced by madder, as the latter always contains purpurin. Madder-dyed fibres are also distinguished by boiling them with a strong solution of alum, when the purpurin is dissolved with formation of a reddish-yellow liquid, which exhibits a strong greenish-yellow fluorescence and characteristic absorption-bands (page 243).

On exposure to nitrous fumes, cloth dyed with alizarin-red becomes orange, from formation of nitro-alizarin.

Fibres dyed with alizarin are but little affected when boiled with ammonia or caustic soda solution of moderate strength. Alizarin red is turned to violet when boiled with baryta water. Dilute acids are almost without action. Concentrated hydrochloric acid decomposes the color lakes, and partially or completely removes the metallic oxides. The violets are more readily affected than the reds, and of the latter turkey-red offers the greatest resistance.

Cold concentrated sulphuric acid dissolves the fibre of cotton as well as the coloring matter. On diluting the solution with water, the alizarin, etc., will be thrown down as a flocculent precipitate, which may be dissolved by agitation with ether. The separated ethereal solution on evaporation will leave a residue, in which alizarin and its associates may be recognized by their appearance on sublimation, the color and absorption-spectra of their alkaline solutions, etc.

Fabrics dyed with alizarin are decolorized when boiled with a mixture of two parts of alcohol and one of strong hydrochloric acid. This reaction distinguishes *alizarin black* from *aniline black*, which latter color is unaffected, or merely turned greenish, by similar treatment. *Logwood blacks*, on the other hand, are destroyed even by dilute acids, which acquire a red color.[1]

Strong acid oxidizing agents, such as nitric acid and ferric chloride, destroy alizarin colors.

Chrysophanic Acid. $C_{15}H_{10}O_4 = C_{14}H_5(CH_3)(OH)_2O_2$. This substance, the nature of which was formerly misunderstood, is now

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[1] To distinguish alizarin black from other blacks on wool, apply to the cloth a few drops of hydrochloric acid and let it stand for ten minutes; if a red color appears it is not alizarin black. If no change is observed add a few more drops of acid and sprinkle it over with a little stannous chloride; after half an hour wash in cold water; if there is any alteration in the color it is not alizarin black.

recognized as a dihydroxy-methyl-anthraquinone, being homologous with c h r y s a z i n (page 234).

Chrysophanic acid occurs ready-formed in rhubarb root, senna leaves, the wall lichen (*Parmelia parietina*), and some other plants, or, at any rate, is readily produced by the oxidation of a substance pre-existing in these plants. This substance has the formula $C_{30}H_{26}O_7$, and is called c h r y s o p h a n or c h r y s a r o b i n, chrysophanic acid being a product of its oxidation, $C_{30}H_{26}O_7 + O_4 = 2C_{15}H_{10}O_4 + 3H_2O$. Many of the statements made as to the occurrence and properties of chrysophanic acid really apply to chrysarobin.

The best source of chrysophanic acid is the commercial product known as *chrysarobin*,[1] or Goa powder,[2] which consists of the medullary matters of the stem and branches of *Andira araroba*, a plant growing in the neighborhood of Bahia. The Goa powder is exhausted by boiling benzene or petroleum spirit, conveniently in a Soxhlet-tube. The filtered liquid, after concentration if necessary, deposits on cooling pale yellow, warty crystals. These may be purified by repeated crystallization from glacial acetic acid, when the substance is obtained in small yellow laminæ.

Pure chrysophanic acid may be prepared from the chrysophan or chrysarobin obtained as above by pouring a somewhat dilute solution of caustic alkali over the substance contained in a large retort, and then passing a current of air over the surface of the liquid (L i e b e r m a n n and S e i d l e r, *Pharm. Jour.* [3], ix. 897). The retort is agitated so as to renew the surface, and the operation continued until the chrysarobin is dissolved, and the

[1] The *German Pharmacopœia* (1890) indicates as chrysarobin a body with the following characters:—A crystalline powder, yellow and very light; boiled with 2,000 parts of water, it does not dissolve completely, but gives a yellowish solution, giving no reaction with litmus or ferric chloride. Solution of ammonia in contact with chrysarobin for a few days becomes of a carmine color. One milligramme of the substance treated with a drop of fuming HNO_3 gives a red color, becoming violet with ammonia. It dissolves in 150 parts of boiling alcohol, in warm chloroform and in CS_2. Chrysophanic acid, when pure, on the other hand, occurs in yellow clinorhombic prisms, melting at 162°, insoluble in water, soluble in 224 parts of boiling alcohol. A characteristic reaction is the addition of a few drops of H_2SO_4 when a red tint is found, which turns blue on the addition of KOH.

[2] In the *British Pharmacopœia* of 1885 the natural product Goa powder is confounded with the crystalline principle extracted therefrom by solvents, "*chrysarobinum*" being described as "medullary matter," and at the same time "minutely crystalline."

solution has acquired uniformly the red color characteristic of an alkaline solution of chrysophanic acid. The liquid is then treated by an acid, and the precipitate washed, dried, and exhausted with petroleum spirit (not benzene) in a Soxhlet-tube. On cooling, the chrysophanic acid is obtained in beautiful yellow laminæ.

The following are the chief differences between chrysarobin and chrysophanic acid:—

	Chrysarobin.	Chrysophanic Acid.
Action of ammonia.	Insoluble.	Soluble with red color.
Action of very dilute caustic potash solution.	Undissolved at first. On agitation with air, dissolves with red color.	Soluble with red color.
Action of strong caustic potash solution.	Soluble with yellow color and strong green fluorescence. On exposure to air, color changes rapidly to red.	Soluble with red color.
Action of fusing caustic potash.	Brown coloration.	Blue coloration.
Action of concentrated sulphuric acid.	Soluble with yellow color.	Soluble with red color.

The chrysophanic acid of commerce consists of an indefinite mixture of chrysopban or chrysarobin with the true chrysophanic acid which is the product of its oxidation.[1]

According to J. A g e m a, commercial chrysophanic acid may be purified by dissolving it in chloroform and adding an equal volume of rectified spirit, when the pure acid only is precipitated.

Chrysophanic acid crystallizes in golden yellow scales or prisms. It melts at 178° C., and sublimes at a higher temperature with partial decomposition. Exposure to a temperature of 195° converts chrysophanic acid into a body allied to purpurin, which colors alum mordants pomegranate-red and iron mordants a light greenish-blue. It is nearly insoluble in water, but dissolves sparingly in hot alcohol (1 in 224), the greater part separating on cooling. Chrysophanic acid is also readily soluble in ether, chloroform, benzene, petroleum spirit, amylic alcohol, and glacial acetic acid, the solutions being yellow or brownish-yellow.

[1] A great deal of the chrysophanic acid of commerce is chrysarobin, with very small quantities of chrysophanic acid. The pure acid melts at 178° C., and forms small leaflets, of the formula $C_{15}H_{10}O_4$. It is not hygroscopic, and dissolves in strong sulphuric acid, with a deep red color. When heated with hydriodic acid, a body, termed chrysophanhydranthone, $C_{15}H_{12}O_3$ is formed, crystallizing from alcohol in yellow leaflets.

When treated with a solution of caustic alkali or ammonia, chrysophanic acid dissolves readily, forming a liquid which is pink when very dilute, and dark purplish-red in a more concentrated state. The chrysophanic acid is precipitated in yellow flakes on neutralizing the alkaline liquid. A very small quantity of alkali suffices for the production of the red color. If the red solution of chrysophanic acid in caustic alkali be evaporated to dryness, it turns violet and **blue** during the operation. The films deposited on the sides of the vessel especially exhibit this change of color.

If a solution of chrysophanic acid in ether, chloroform, benzene, amylic alcohol, or petroleum spirit be shaken with solution of soda, the coloring matter passes completely or partially into the aqueous liquid, which it colors pink or crimson. Ammonia gives the same reaction as soda with a solution of chrysophanic acid in ether or petroleum spirit, but does not readily extract the coloring matter from its solution in chloroform or benzene.

The acid characters of chrysophanic acid are but feebly marked. It forms unstable barium and lead salts, which are decomposed even by carbonic acid. An ammoniacal solution of chrysophanic acid is precipitated lilac by acetate of lead and rose-color by alum.

Chrysophanic acid is not acted on by dilute nitric acid, but the strong acid converts it into t e t r a n i t r o - c h r y s o p h a n i c a c i d, $C_{15}H_6(NO_2)_4O_4$, a body homologous with c h r y s a m i c a c i d, obtained by the action of nitric acid on aloes or chrysazin.

When heated with acetic anhydride and acetate of sodium, chrysophanic acid yields a d i a c e t y l - d e r i v a t i v e.

When heated with zinc-dust, chrysophanic acid is reduced to m e t h y l - a n t h r a c e n e, $C_{15}H_{10}$, just as alizarin and chrysazin yield a n t h r a c e n e, $C_{14}H_8$, when similarly treated.

Chrysophanic acid possesses decided antiseptic properties, and has proved of service in the treatment of certain forms of skin-disease. It is said to be somewhat uncertain in its action, a fact which is not improbably due to an admixture of chrysarobin, to the deoxidizing action of which impurity it has been suggested that the chrysophanic acid of commerce owes its chief value.[1]

[1] Working on this idea, Liebermann (*Pharm. Jour.* [3], xviii. 741, 780) has attempted to reduce chrysophanic acid to chrysarobin by treatment with zinc-dust and ammonia. He obtained instead a *leuco-derivative*, the lower homologue of which, prepared from alizarin and purpurin in a similar manner, is now commercially known as a n t h r a r o b i n (page 237).

Chrysophanic acid is said to produce purplish-brown stains on linen or cotton, which are only removable with difficulty, prolonged immersion of the fabric in a solution of bleaching-powder being the best mode of treatment. The author has not succeeded in producing these stains except in the presence of an alkali. A solution of chrysophanic acid in alcohol, acetic acid, or petroleum spirit merely colors linen a light yellow color. On washing the stained fabric with soap, the purplish-brown stain is readily developed.[1]

An aqueous or alcoholic solution of chrysophanic acid does not dye silk or wool yellow.

Chrysophanic acid is said to be liable to adulteration with picric acid and other yellow coloring matters. Inorganic admixtures may be detected by igniting a portion of the sample. *Picric acid*, if present, would be detected by the yellow coloration the sample imparts to cold water; by the yellow crystalline precipitate produced on adding potassium carbonate to the alcoholic solution of the sample; and by immersing a piece of white wool in the hot aqueous solution, which, in presence of picric acid, will be dyed yellow. *Aurin* or *rosolic acid* might be detected in chrysophanic acid by treating the sample with chloroform or benzene, which would dissolve the chrysophanic acid without affecting the admixture.

The extraction of the chrysarobin or chrysophanic acid present in plant-products may be effected by treating the powdered substance with the ether, benzene, or petroleum spirit, in the manner already described. Goa powder yields from 70 to 80 per cent. of the active principle, while the proportion of chrysophanic acid contained in rhubarb is but small. According to D r a g e n d o r f f, the presence of chrysophanic acid in a condition (free) extractable by cold petroleum spirit is a test of the quality of rhubarb. Good rhubarb yields a colorless extract even when left for several days in contact with petroleum spirit, while a rhapontic rhubarb yields an intensely yellow extract. According to R o c h l e d e r (*Chem. News*, xx. 78), the acid from rhubarb generally contains e m o d i n, $C_{15}H_{10}O_5$. This body has the constitution of a tri-hydroxymethyl-anthraquinone, and hence is homologous with purpurin. It occurs to a notable extent in the bark of *Rhamnus frangula*, and may be

[1] Evidently, the production of chrysophanic acid stains on linen may be avoided by dissolving out the coloring matter and grease with benzene.

separated from chrysophanic acid by means of sodium carbonate, which dissolves the emodin only, with blood-red coloration. It forms long, brittle, monoclinic prisms, melting at 245°–250°, and is converted into methyl-anthracene by heating with zinc-dust.

A body having considerable analogy to chrysophanic acid occurs in the root of the Mexican plant *Trixis pipitzahuac* or *Perezia fructicosa*. This substance, which has been named p i p i t z a h o i c a c i d, has the formula $C_{15}H_{20}O_3$, and dissolves in alkalies with a color resembling that of potassium permanganate (A n s c h ü t z and L e a t h e r, *Jour. Chem. Soc.*, xlix. 709).

6. Diphenylmethane and Triphenylmethane Coloring Matters.

D i p h e n y l m e t h a n e, $CH_2 \begin{cases} C_6H_5 \\ C_6H_5 \end{cases}$, and t r i p h e n y l m e t h a n e,

$CH \begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{cases}$ form the starting point of a large number of important dyestuffs. The numerous derivatives of the aurins, phthaleins, and rosanilines may be classified under these two parent substances.

Diphenylmethane gives rise to a few important dyestuffs, such as the auramines and pyronines, by the introduction of amido- and alkyl-groups occupying the para-position to each other. The real starting point for these dyestuffs is *tetramethyldiamidobenzophenone*, which has the formula $CO <^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}$. This body is prepared by the action of carbonyl chloride on dimethylaniline in the presence of aluminium chloride:

$$COCl_2 + 2C_6H_5N(CH_3)_2 = 2HCl + CO <^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}.$$
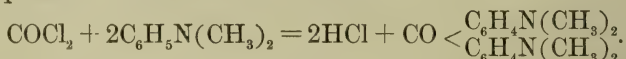
The crystalline paste so obtained is heated on a water-bath until the reaction is completed. The salt is purified by dissolving in hydrochloric acid and reprecipitating with caustic soda. Tetramethyldiamidobenzophenone crystallizes in the form of colorless plates, melting at 174° C., insoluble in water, but readily soluble in ether and hot alcohol. By the action of nascent hydrogen on this body, it is converted into a corresponding carbinol, $^{(CH_3)_2N.C_6H_4}_{(CH_3)_2N.C_6H_4} > CH.OH$, which forms blue-colored salts with acids.

Auramine, $C_{17}H_{21}N_3.HCl + H_2O$. When tetramethyldiamido-benzophenone is heated with ammonium chloride and zinc chloride to 150°–160° C., it reacts to form an i m i d o - t e t r a - m e t h y l - d i a m i d o - d i p h e n y l m e t h a n e. The reaction is represented by the following equation:—

$$CO \begin{cases} C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2 \end{cases} + NH_3 = C \begin{cases} C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2 \\ :NH \end{cases}$$
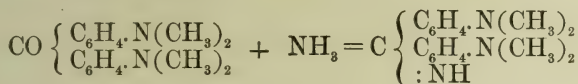
The new body is a colorless base, which forms salts of an intensely yellow color, the h y d r o c h l o r i d e being the *auramine* of commerce. The hydrochloride, sulphate, and acetate are readily soluble in water, but the thiocyanate and double zinc salt are only very sparingly soluble in cold water.

Commercial auramine is a sulphur-yellow powder, which dissolves somewhat sparingly in cold, but more readily in hot water, to form a bright yellow solution. It is also soluble in alcohol. The cold aqueous solution is unchanged by hydrochloric acid, but on boiling the liquid is decolorized, with re-formation of ammonium chloride and tetramethyl-diamido-benzophenone. On addition of caustic soda, the aqueous solution of auramine yields a white precipitate of the free base. The precipitate dissolves on agitation with ether, and the separated ethereal solution is not fluorescent, but communicates a yellow color to acetic acid when shaken with it. When treated with zinc and acetic acid, auramine gives an evanescent green coloration. Alkaline reducing agents, such as sodium amalgam or zinc and ammonia, gradually decolorize the alcoholic solution of auramine, and on adding water a colorless reduction-product is precipitated, which when heated with acetic acid yields a deep blue color. With strong sulphuric acid it yields a colorless solution, which on dilution with water, becomes yellow in color.

Auramine produces a brilliant and very pure yellow when mordanted on cotton with alizarin oil or tannin and a salt of antimony.[1] The fibre is decolorized both by acids and alkalies.

Auramine sometimes occurs in commerce mixed with magenta

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[1] Auramine is one of the few artificial yellow dyes which can be fixed on the fibre by means of tannin. Hence it may be employed to produce very yellow shades of malachite green on cotton. When using auramine the temperature of the dyebath must not be above 160° F., as the dyestuff is decomposed above that temperature.

under the name of F u c h s i n e S c a r l e t, and with safranine as
S a f r a n i n e S c a r l e t.

Auramine dyes textile fibres mordanted with tannin a greenish-
yellow which is fairly fast to washing and light, but very sensi-
tive to chlorine. Auramine is also used to a considerable extent
in paper staining and leather dyeing.

Several brands of auramine are prepared for commerce, the pure
quality bearing the name of A u r a m i n e O; other qualities con-
taining more or less dextrin appear under the names A u r a m i n e
I, II, or III.

If in the manufacture of auramine the ammonium chloride be
replaced by the hydrochlorides of aniline, xylidine, naphthyla-
mine, etc., s u b s t i t u t e d a u r a m i n e s are obtained, none of
which appear to crystallize, and which dye shades ranging from
yellow to light brown.

Auramine G, is a dyestuff analogous to auramine; it possesses
the formula:

$$(NH_2)C \begin{cases} (1)\ C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.CH_3 \end{cases} \\ (1)\ C_6H_3 \begin{cases} (4)NH.(Cl).CH_3 \\ (3)CH_3 \end{cases} \end{cases}$$
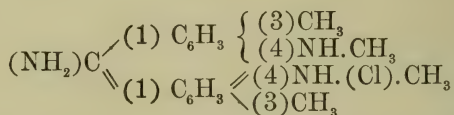
It is, therefore, the hydrochloride of amido-dimethyl-diamido-
diortho-tolyl-methane.   It is a derivative of dimethylditolyl-
methane, and is prepared in a manner analogous to that employed
for the preparation of auramine.   It is a yellow powder soluble in
water with a yellow color.   The aqueous solution treated with
sodium hydrate gives a flocculent precipitate which dissolves in
ether, and the separated ethereal solution communicates a yellow
color to acetic acid when shaken with it.   Hydrochloric acid
added to the aqueous solution causes no change in color, but on
boiling the solution is decolorized, due to the re-formation of am-
monium   chloride   and   dimethyldiamido-diortho-ditolyl-ketone.
With strong sulphuric acid auramine G yields a colorless solution,
which becomes a pale yellow on dilution with water.   Auramine
G is dyed in a manner similar to that of Auramine O, but yields a
greener shade of yellow.

By the condensation of dimethyl-meta-amidophenol with for-
maldehyde an oxide of tetramethyl-diamido-diphenylmethane is
obtained, which on oxidation yields a carbinol possessing the
formula:

$$CH\underset{\displaystyle C_6H_3-N(CH_3)_2}{\overset{\displaystyle C_6H_3=N(Cl)(CH_3),}{>O}}$$
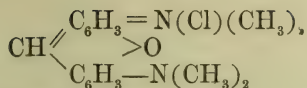
This body is a derivative of diphenyl-methane and is called P y r o n i n e G. It is a red dyestuff somewhat resembling the rhodamines in shade. It occurs in the form of green crystals, soluble in water, giving a red solution having a yellow fluorescence; also soluble in alcohol with a red color and a yellow fluorescence. On treating the aqueous solution with caustic soda a pale red precipitate is produced; the addition of excess of hydrochloric acid causes the color of the aqueous solution to become bright orange. With strong sulphuric acid the dyestuff gives an orange solution, which becomes red on dilution with water.

There is a corresponding tetra-ethyl derivative which is called P y r o n i n e B; its shade is somewhat bluer than the preceding compound, and its fluorescence is redder, otherwise its reactions are similar to those described for pyronine G. The pyronines dye cotton mordanted with tannic acid brilliant bluish-red shades.

Acridine Red 3 B (also B, and BB) is obtained by the oxidation of pyronine B by means of potassium permanganate. It has the formula:

$$HO.C\underset{\displaystyle C_6H_3<N(C_2H_5)_2}{\overset{\displaystyle C_6H_3<\overset{\displaystyle N(Cl)(C_2H_5)_2}{O}}{}}$$
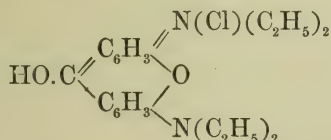
It is a brown powder soluble in water and alcohol, giving a red solution with a yellow fluorescence. Caustic soda added to the aqueous solution produces a red precipitate; the addition of hydrochloric acid changes the color to orange. With strong sulphuric acid the dyestuff gives a yellow solution with a green fluorescence; dilution with water causes the color to change to red.

Acridine red is dyed with a tannin mordant on either cotton or silk in a manner similar to the pyronines, but the shade obtained is more yellow than that produced by the latter. The color is quite fast to washing and light.

T r i p h e n y l m e t h a n e gives rise to a large class of important dyestuffs, including the derivatives of rosolic acid, the phthaleïns, and rosaniline.

By the introduction of hydroxyl- or amido-groups into triphenylmethane in the para-position to that occupied by the methane residue, colorless derivatives known as l e u c o - c o m -

p o u n d s are produced. By the oxidation of these bodies two hydrogen atoms are abstracted and an inner condensation takes place, a linking being established between the methane carbon atom and an oxygen or nitrogen atom of one of the hydroxyl- or amido-groups respectively. P a r a l e u c a n i l i n e, for example, which has the formula:

$$CH \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases}$$
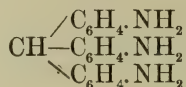
on oxidation condenses to p a r a r o s a n i l i n e, which is represented by:

$$C \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH \end{cases}$$
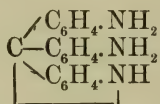
The corresponding hydroxyl compound would be p a r a r o s o l i c a c i d :

$$C \begin{cases} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4O \end{cases}$$
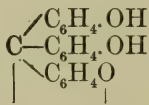
In triphenylmethane dyestuffs, therefore, a closed ring is present, and they contain the chromophor groups $\equiv$ C—NH— or $\equiv$ C—O—. As these dyestuffs appear to exhibit a relationship to the quinones in their properties, their formula is also written in the form $= C = C_6H_4 = NH$. Structurally, the difference between these formulæ is as follows:
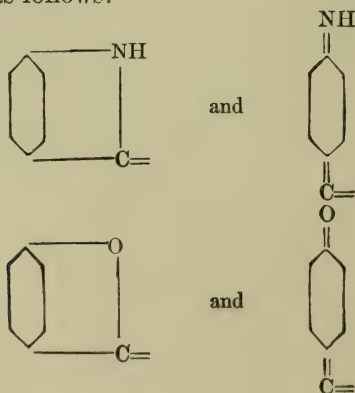
Rosaniline and its Allies.

Rosaniline, a base of which the salts are usually known in commerce as fuchsine and magenta, was one of the first—and still is

one of the most interesting and important—of the basic coloring matters obtained from coal-tar. It is the type of a large number of bodies, not a few of which are or have been of practical importance. Many of them dye silk and wool without the aid of a mordant, and by suitable means they can also be fixed on vegetable fibres.

Rosaniline and its allies are derivatives of the hydrocarbon t r i-p h e n y l m e t h a n e, obtained by the action of benzene on chloroform, in presence of aluminium chloride:—$H.C: Cl_3 + 3C_6H_5.H = 3HCl + (C_6H_5)_3: CH$. By oxidation of the hydrocarbon with chromic acid in glacial acetic acid solution at 100° C., t r i-p h e n y l - m e t h y l   a l c o h o l   or   t r i p h e n y l   c a r b i n o l $(C_6H_5)_3C.OH$, is obtained. On the other hand, when slowly added to cold fuming nitric acid, triphenyl-methane is converted into the t r i n i t r o-derivative, $(C_6H_4NO_2)_3CH$. This may be oxidized by treatment with chromic acid to the corresponding c a r b i n o l, $(C_6H_4NO_2)_3: C.OH$, which when partially reduced by zinc-dust and acetic acid is converted into p a r a r o s a n i l i n e, $(C_6H_4NH_2)_3C.OH$. Hence, pararosaniline has the constitution of a t r i a m i d o t r i p h e n y l - c a r b i n o l,[1] while its homologue r o s a n i l i n e   is   m e t h y l - p a r a r o s a n i l i n e   or   triamido-diphenyl-tolyl-carbinol.

<p style="text-align:center;">*Pararosaniline.*   *Rosaniline.*</p>

$$C \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ OH \end{cases} \qquad \begin{cases} C_6H_3(CH_3)NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ OH \end{cases}$$
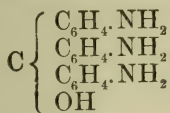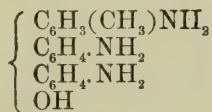
By the action of reducing agents the bases lose oxygen. Thus rosaniline yields l e u c a n i l i n e, $(C_7H_6NH_2)(C_6H_4NH_2)_2: CH$, and pararosaniline the lower homologue t r i a m i d o - t r i p h e n y l - m e t h a n e, $(C_6H_4NH_2)_3: CH$. The salts of the bases are colorless.

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[1] This formula, which gives the rosaniline bases the constitution of a carbinol, does not seem to be in agreement with the fact that such carbinols are strong bases and yield stable salts with one molecule of an inorganic acid; for these leuco bases require as many as three molecules of acid in some cases. W e i l (Ber. xxviii. p. 205) has proposed the formula:

$$C \begin{cases} \overset{\displaystyle (C_6H_4NH_2)_2}{\underset{\displaystyle C_6H_4.NH_3}{}} \\ \end{cases}$$
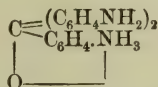
for these bases which appears to be more in accordance with observed facts.

Pararosaniline and rosaniline are well-defined bases which react with acids to form salts, with elimination of the elements of water. Thus with hydrochloric acid, rosaniline reacts in the following manner:—$C_{20}H_{21}N_3O + HCl = C_{20}H_{19}N_3.HCl + H_2O$. In constitutional formulæ the reaction must be expressed as follows:[1]

$$HCl + C \begin{cases} C_6H_3(CH_3).NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ OH \end{cases} = H_2O + C \begin{cases} C_6H_3(CH_3).NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2.Cl \end{cases}$$
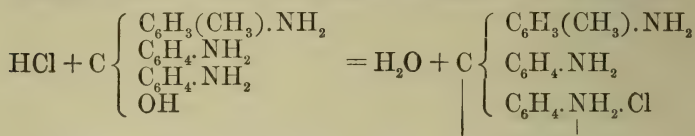
All the amido-derivatives of di- and triphenyl-carbinol react similarly with acids.

On account of this peculiar behavior, the constitution of rosaniline and its allies was formerly misunderstood, but for representing many of their reactions the formulæ of the anhydrides may be conveniently used.

When a mixture of one molecule of para-toluidine with two of aniline is treated with an oxidizing agent of moderate power, such as arsenic acid or mercuric chloride or nitrate, p a r a r o s a n i l i n e results; and when a molecule of ortho-toluidine is substituted for the second molecule of aniline, r o s a n i l i n e is produced, according to the equation :—$CH_3(4)C_6H_4.(1)NH_2 + C_6H_5.NH_2 + CH_3$ $(2)C_6H_4(1)NH_2 + O_3 = C_{20}H_{21}N_3O + 2H_2O$.

By treatment with nitrous acid, rosaniline and pararosaniline are converted into r o s a u r i n and a u r i n respectively, while, on the other hand, by heating rosaurin and aurin to 120° with strong ammonia the reverse action occurs, and rosaniline and pararosaniline are respectively obtained.

Rosaniline and pararosaniline are themselves colorless, but their salts are remarkable for the intense crimson-red color of their solutions. Rosaniline hydrochloride forms the commercial dye known as *magenta* or *fuchsine;* while *acid magenta* is a mixture of the sodium salts of several rosaniline-sulphonic acids.[2]

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[1] The formula for rosaniline hydrochloride given in the text shows one nitrogen atom as exercising pentavalent functions, and is generally regarded as the most probable. An alternative view of the constitution of magenta is:—

$$C \begin{cases} C_6H_3(CH_3).NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ Cl \end{cases}$$
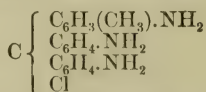
[2] A. Rosenthiel (Comptes Rend. cxvi. 194) has studied the constitution of rosaniline from a very pure material obtained by treating the dry coloring matter with hydrochloric or hydrobromic acid gas, and subsequently exposing the prod-

From the residues of the manufacture of rosaniline the less hydrogenized bases **c h r y s a n i l i n e,** $C_{19}H_{15}N_3$, and **c h r y s o -**

ucts over sulphuric acid *in vacuo* for several days. He concludes that rosaniline and its congeners present to acids two distinct properties: they are mainly alcohols, but are also basic, and stand midway between alkaline bases and alcohols. Rosaniline itself is no triamine, but the coloring matters derived from it are the ethereal salts of tertiary amido-alcohols of the aromatic series. This same writer, in the Bull. Soc. Ind. de Mulhouse, 1893, 195, through an investigation of the acid salts of magenta has arrived at the following conclusions:

Hoffman's rosaniline tri-hydrochloride, $C_{20}H_{19}N_3.3HCl$, possesses the empirical formula $C_{20}H_{23}N_3Cl_4$, but as a matter of fact, it does not exist, and the hypotheses based upon it must be abandoned, especially—(1.) The formula $C_{20}H_{19}N_3$ for rosaniline anhydride. (2.) E. and O. Fischer's formula for its lower homologue—

$$(N_2H.C_6H_4)_2 = C - C_6H_4$$
$$\diagdown \diagup$$
$$NH$$
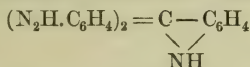
(3.) The existence of a double bond between one of the nitrogen atoms and the carbon of the methane and phenylene. (4.) This double bond not existing, it can no longer be considered the cause of the dyeing power in magenta and similar dyes. Accordingly the formula of magenta must be $Cl - C \equiv (C_6H_4.NH_2)_3$, and magenta must be considered as the hydrochloric ester of a tri-amido alcohol. In combination with acids this alcoholic function of magenta first comes into play. It is invariably modified in the presence of amido-groups, the basic nature of which is superadded to the feebly basic $\equiv COH$ group and imparts to the OH group of the rosaniline, or to the Cl of magenta, as great a capacity for ready chemical interchange as is observable in any metallic salt. The hydrochloric ester of rosaniline, *i. e.*, magenta, being formed, any excess of acid is fixed by the amido-groups and the molecule is saturated when all the amido-groups have become neutralized—

$$Cl - C \equiv (C_6H_4.NH_2)_3.3HCl.$$

The presence of the acid radical in the methane carbon also explains the lack of stability observable in the acid salts of magenta. An analogous decrease of the basic properties is noticeable in chlorinated, brominated, or nitrated aniline. A glance at the formulæ of leucaniline and magenta at once explains now why the former yields stable stalts while the salts of the latter decompose so easily—

$$H - C \equiv (C_6H_4.NH_2)_3, \quad Cl - C \equiv (C_6H_4.NH_2)_3.$$
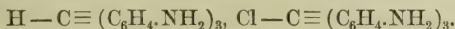
The hydrogen atom preserves the basicity of the molecule, whereas the chlorine atom of the magenta weakens it. The relation existing between the colorless and the colored derivatives of triphenylmenthane is clearly explained in the following formulæ:—

$$Cl - C \equiv H_3 \qquad\qquad Cl - C \equiv (C_6H_5)_3.$$
Methyl chloride.   Triphenylmethane chloride.
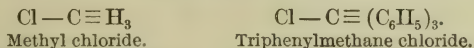
These two compounds are colorless.

Triamidotriphenylmethane chloride (magenta)—

$$Cl - C \equiv (C_6H_4.NH_2)_3.$$

Without going so far as to ascribe the dyeing power to the presence of the amido-groups, it may be said that the coloring matters in question are the esters of aromatic amido alcohols.

t o l u i d i n e, $C_{20}H_{17}N_3$, are also obtainable. They are remarkable for forming almost insoluble nitrates, and the hydrochlorides constitute the commercial product known as *phosphine* or aniline orange. *Safranine* and the *indulines* are also secondary products of the manufacture of rosaniline.

By heating a salt of rosaniline with aniline, one, two, or three atoms of hydrogen in the original base may be replaced by the radical phenyl, with the formation of m o n o-, d i-, or lastly, t r i-p h e n y l r o s a n i l i n e, $C_{20}H_{18}(C_6H_5)_3N_3O$. These substituted products become more intensely blue with each replacement of the hydrogen atoms, so that the salts of the mono-derivative are reddish-violet, those of diphenyl-rosaniline bluish-violet, while the triphenylated base yields salts of a nearly pure blue.

The dye known as *diphenylamine-blue* is of similar constitution to Paris blue, being the hydrochloride of t r i p h e n y l p a r a r o s-a n i l i n e. It is obtained by heating diphenylamine with oxalic acid:—$3(C_6H_5)_2NH + C_2H_2O_4 = 3H_2O + CO + C_{19}H_{14}(C_6H_5)_3N_3$. The dye *azuline*, obtained by heating aurin with aniline and benzoic acid is apparently an impure kind of diphenylamine blue. By the action of methyl chloride or ethyl chloride on diphenylamine blue, or by using methyl- or ethyl-diphenylamine in the process of manufacture, substitution-products are obtained, the hydrochlorides of which are known in commerce as *methyl blue* and *ethyl blue*. They dye a purer blue shade than the unsubstituted diphenylamine blue. If a mixture of diphenylamine (phenylaniline) and phenyltoluidine (instead of the former base only) be heated with oxalic acid or carbon hexachloride, t r i p h e n y l r o s-a n i l i n e, $C_{20}H_{16}(C_6H_5)_3N_3$, is obtained.

Just as several of the atoms of rosaniline and pararosaniline may be replaced by phenyl or tolyl, so may the radicals ethyl or methyl be substituted for one, two, or three atoms of the hydrogen in rosaniline. The replacement is effected by heating magenta or free rosaniline with alcoholic potash or soda and chloride or iodide of methyl. The *Hofman's violets* so obtained range from RRR, the very red, which is chiefly a salt of m o n o m e t h y l - r o s a n i-l i n e, $C_{20}H_{20}(CH_3)N_3O$, to BBB, the bluest shade, consisting of the highest substitution-products.[1] Similar, but not identical, dyes may be obtained by introducing the methyl or ethyl radical into

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[1] It is a curious fact that while the substituted rosanilines become bluer with each replacement of the hydrogen atoms by phenyl, tolyl, methyl, or ethyl, the color of the substituted *mauveines* follows the reverse rule.

aniline or diphenyl-amine before submitting the latter to the action of oxidizing agents. *Methyl violet* is thus produced.

The coloring matter known as *malachite green* or benzaldehyde green differs from all the preceding in the fact that only two instead of all three of the phenyl groups of the triphenyl carbinol are amido-substituted. Thus malachite green is a salt of t e t r a-m e t h y l - d i a m i d o - t r i p h e n y l - c a r b i n o l, and *brilliant green, helvetia green, fast green, resorcin purple* have an allied constitution.

Many of the basic coloring matters of the rosaniline group are convertible into more readily applicable dyes by s u l p h o n a-t i o n. The sulphonated dyes thus obtained are readily soluble, and dye silk and wool in acid baths. Usually they are not readily fixed on cotton, except *alkali blue*, in which the basic character of the Paris blue from which it is derived is not wholly destroyed by conversion into a mono-sulphonic acid.

In some cases, as in that of *acid magenta*, the sulphonated dye retains the hydroxyl group of the rosaniline from which it is derived, and hence is of the carbinol type. In other cases, as for instance in *alkali-blue*, the sulphonated dye appears to lose the elements of water, just as the basic dye does on combining with an acid. This is illustrated by the following examples, which suffice to indicate the formulæ of the whole class:—

<table>
<tr><td align="center">*Acid Magenta.*
odium salt of Rosaniline-
trisulphonic acid.[1]</td><td align="center">*Alkali Blue.*
Sodium salt of Triphenyl-rosaniline-
monosulphonic acid.</td></tr>
</table>
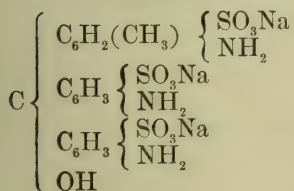
$$C\begin{cases} C_6H_2(CH_3) \begin{cases} SO_3Na \\ NH_2 \end{cases} \\ C_6H_3 \begin{cases} SO_3Na \\ NH_2 \end{cases} \\ C_6H_3 \begin{cases} SO_3Na \\ NH_2 \end{cases} \\ OH \end{cases} \qquad C\begin{cases} C_6H_2(CH_3). \begin{cases} SO_3Na \\ NH(C_6H_5) \end{cases} \\ C_6H_4.NH(C_6H_5) \\ C_6H_4.N.(C_6H_5) \end{cases}$$
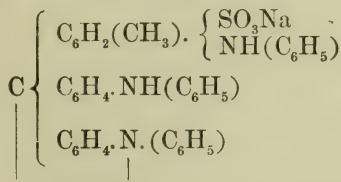
The coloring matters of the rosaniline group may be conveniently

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[1] According to Benedikt, acid magenta is a mixture of the sodium salts of mono- and disulphonated rosaniline. According to Prud'homme, commercial acid magenta, according to the proportion of acids employed in its manufacture, is a mixture of the colorless—

$$HO - C \equiv [C_6H_3.SO_3Na.NH_2]_3$$

and of the colored—

$$Cl - C \equiv [C_6H_3.SO_3Na.NH_2]_3$$

18

classified as aniline red, aniline blues, aniline violets, aniline greens, and associated dyes. This arrangement will be adopted in their description.

Rosaniline. Aniline Red. Triamidotolyl-diphenyl-carbinol. $C_{20}H_{21}N_3O = (C_6H_4NH_2)_2(C_7H_6NH_2)COH$.

Rosaniline is the artificial organic base the salts of which form the magnificent dyeing materials known as *aniline-red, magenta, fuchsine, azaleine, rubine, roseine, solferino, erythrobenzene,* and by other more fanciful names. The coloring matter is produced whenever a mixture of aniline and toluidine is heated to about 180° C. with an oxidizing agent of moderate power. A. W. H o f-m a n n showed that the presence of both aniline and toluidine—which coexist in commercial aniline oils—was essential to the production of the color, and represented the reaction thus:—$C_6H_7N + 2C_7H_9N + O_3 = C_{20}H_{19}N_3 + 3H_2O$. The more recent researches of E. & O. F i s c h e r have shown that the free base contains oxygen, and on reacting with acids loses the elements of water.

A great number of methods of oxidizing aniline oil for the production of rosaniline have been employed and patented, but only three are in general use, namely: the arsenic acid, the mercuric nitrate, and the nitrobenzene processes.[1] According to the oxidiz-

[1] According to the *arsenic acid process,* 100 parts of "aniline oil for red" are heated with 128 parts of arsenic acid of 75° Baumé for eight hours to a tempera-ture somewhat exceeding the boiling point of aniline, in a boiler fitted with a con-densing tube. Water and a part of the aniline employed distil over. The resi-due is boiled with water, and the liquid filtered from the insoluble matter, which contains m a u v a n i l i n e , v i o l a n i l i n e , and some c h r y s a n i l i n e . The so-lution, which contains arseniate and arsenite of r o s a n i l i n e , c h r y s a n i l i n e , excess of arsenic acid, and resinous substances, is treated with a large excess of common salt. Sodium arsenite and arseniate and rosaniline hydrochloride are formed, and the last of these, being sparingly soluble in strong brine, separates out. The precipitated coloring matter is dissolved in water and purified by crys-tallization or again precipitated by the addition of salt. The mother-liquors yield an impure magenta, known as *cerise* or *geranium.* The arsenic is recovered by treating the waste-liquors with lime, when arsenite and arseniate of calcium are precipitated. The resinous matters may be used for the production of the color-ing matters known as *grenadin* and *maroon.*

A very pure nitrate of rosaniline may be obtained by oxidizing aniline oil with *mercuric nitrate,* and this may be converted into the hydrochloride by double decomposition with common salt.

Instead of using arsenic acid, *nitrobenzene* and ferrous chloride are sometimes employed. The latter body is oxidized by the nitrobenzene, and the product in turn oxidizes the aniline, so that it acts as a carrier of oxygen. 100 parts of ani-line oil are treated with two-thirds of the amount of hydrochloric acid required

ing agent employed, and the subsequent treatment, the product may be the hydrochloride, nitrate, acetate, or other salt of rosaniline, but the first is now by far the most commonly met with.

Free rosaniline can be obtained by precipitating a solution of either of the commercial salts of rosaniline by excess of ammonia. If a boiling solution of the hydrochloride be employed, a reddish crystalline precipitate is produced, and the colorless liquid deposits on cooling a further crop of crystals of the pure base in colorless needles and plates, which have the composition $C_{20}H_{21}N_3O$ or $C_{20}H_{19}N_3H_2O$.

Rosaniline is a non-volatile, colorless, bitter substance. Heated in boiling water it melts, and dissolves to the extent of 0.3 per cent., a portion being deposited on cooling. In alcohol it dissolves in the proportion of about 1 per cent. In ether, rosaniline dissolves to form a colorless solution, which dyes silk crimson, and gives a fine crimson color on agitation with dilute acetic acid. In benzene, rosaniline is said to be insoluble, but is very soluble in aniline.

Rosaniline loses no water at 100° C. When heated alone to about 130°, it is decomposed. If the free base or one of its salts be heated with water under pressure to about 240° C., phenol and ammonia are produced, with other products; but if the water be acidulated with hydrochloric acid, or if the rosaniline be heated with concentrated hydriodic acid, it is completely resolved into aniline and toluidine.

SALTS OF ROSANILINE. Rosaniline is a well-defined and powerful base, capable of combining with either one, two, or three equivalents of an acid. The t r i - a c i d s a l t s are brownish-yellow, both in the solid state and in solution, and are readily soluble in water and alcohol. The d i - a c i d s a l t s are little known and difficult to prepare. The m o n o - a c i d salts, typified by ordinary *magenta*, are the most interesting and important. They are stable crystalline bodies having a beetle-green metallic lustre, and are mostly soluble in water and alcohol, forming violet-red, non-

for neutralization, and 50 parts of nitrobenzene added. The mixture is heated, while from 3 to 5 parts of iron filings are gradually added. The subsequent operations are the same as in the arsenic acid process. The bye-products contain much i n d u l i n e, but no chrysaniline.

A valuable article on the manufacture of magenta has been published by P. S c h o o p in *Dingler's Polytechnische Journal*, cclviii. 276, and translated in *Jour. Soc. Dyers, etc.*, ii. 118.

fluorescent solutions of high tinctorial power. Their solutions
dye silk and wool a magnificent crimson color, without the aid of
a mordant, and by proper means the color may be fixed on vege-
table fibres. Formerly, English-made *magenta* was generally ros-
aniline acetate; the French article known as *roseine* consisted of
the hydrochloride; while the nitrate was known as *rubine* or *aza-
leine.*

Rosaniline Acetate, $C_{20}H_{19}N_3,C_2H_4O_2$, forms magnificent crystals
with a beetle-green reflection, which are apt to turn brownish-red.
It is one of the soluble of the salts of rosaniline, and also dissolves
freely in alcohol. The acetate was formerly the most commonly
occurring salt of rosaniline, but latterly has been superseded by
the hydrochloride.

Rosaniline Chromate is a brick-red, nearly insoluble powder.

Rosaniline Hydrochloride, or hydrochlorate of rosaniline,
$C_{20}H_{19}N_3,HCl$. This compound, which constitutes the ordinary
magenta, fuchsine, or *roseine* of commerce, crystallizes in very
small, deliquescent rhombic plates, which are somewhat sparingly
soluble in pure water, but more readily in acidulated water and in
alcohol. It is also soluble in amylic alcohol, but insoluble in
ether. Rosaniline hydrochloride combines with platinic chloride
to form an uncrystallizable c h l o r o p l a t i n a t e. With concen-
trated hydrochloric acid, rosaniline hydrochloride yields brown
needles of the t r i a c i d s a l t, $C_{20}H_{19}N_3,3HCl$. This body dis-
solves in a little water with brown color, but on dilution splits up
into hydrochloric acid and the mono-acid salt, the re-formation of
which is indicated by the change of the color of the solution to
crimson.[1]

Rosaniline Nitrate, $C_{20}H_{19}N_3,HNO_3$, constitutes the commercial
products known as *azaleine* and *rubine.* It is not often met with.

Rosaniline Picrate forms magnificent reddish needles, nearly
insoluble in water.

Rosaniline Sulphate much resembles the hydrochloride.

Rosaniline Tannate has a practical importance in dyeing, as its
insolubility in water affords a means of fixing the coloring matter
on vegetable fibres, and of recovering rosaniline from spent dye-
liquors. It dissolves in alcohol, wood spirit, and acetic acid.

Magenta. Fuchsine. ANILINE RED. These names, as also

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[1] N e w M a g e n t a (I s o r u b i n) is the hydrochloride of tritolylcarbinol. It is
prepared by the condensation of formaldehyde with orthotoluidine. It resembles
magenta in appearance, but is more soluble in water and dyes a bluer shade.

rubeine, roseine, azaleine, etc., are used to signify the salts of rosaniline as occurring in commerce. Formerly, the English-made product generally consisted of r o s a n i l i n e a c e t a t e, and was known as *magenta;* the French article called *roseine* consisted of the h y d r o c h l o r i d e; while the n i t r a t e was known as *rubeine* or *azaleine.*[1] Now the hydrochloride has to a great extent superseded the acetate and nitrate of rosaniline, and the distinction is no longer observed. The following reactions are common to all the commercial varieties of magenta.

Magenta usually occurs in beetle-green crystals or as a dark-green crystalline powder. It dissolves in water with magnificent crimson color without fluorescence. The dilute aqueous and alcoholic solutions of magenta exhibit characteristic absorption-spectra, having a well-defined black band between the Fraunhöfer lines D and E.

Solutions of magenta dye silk and wool without a mordant. The coloring matter is partially removed by boiling water, while soap removes it completely.

Caustic alkalies, ammonia, baryta, lime and magnesia decompose solutions of magenta, free rosaniline being precipitated in a crystalline and nearly colorless state. If magnesia be used,[2] and the operation conducted in a boiling hot liquid, so that some of the liberated rosaniline may remain in solution, and the liquid be then filtered out of contact with air, a colorless filtrate is obtained. On passing carbon dioxide, or the air exhaled from the lungs, through this colorless solution of rosaniline, a crimson coloration is produced, owing to the formation of r o s a n i l i n e

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[1] *Magenta-violet* or *fuchsine V* is a mixture of rosaniline and mauvaniline hydrochlorides.

Cerise is a coloring matter containing magenta, and is used in dyeing browns. The mother-liquors from which magenta has been salted out contain phosphine, unprecipitated magenta, and a brown coloring matter. They are treated with milk of lime, and the precipitate separated. dissolved in acidulated water, and salted out. The cerise obtained forms an amorphous brown mass, with a vitreous fracture.

Maroon and *grenadin* are brown coloring matters obtained by purifying the resinous matters formed in the manufacture of magenta.

Cardinal and *amaranth* consist of mixtures containing magenta as the chief constituent.

[2] If one of the other bases mentioned in the text be substituted for magnesia, it should be added gradually, and only in sufficient quantity to effect exact decomposition, as indicated by the decolorization of the solution.

c a r b o n a t e.   The reaction constitutes a delicate test for carbon dioxide.[1]

If a solution of magenta be treated with excess of soda or ammonia and then agitated with ether, the liberated rosaniline dissolves.   The separated ethereal solution is colorless, but dyes silk a fine crimson, and on shaking with dilute acetic acid yields a crimson solution.

Excess of strong hydrochloric acid turns magenta solutions yellow or brown, owing to the formation of a t r i a c i d   s a l t, which is decomposed on copious dilution, or on adding a solution of sodium acetate, with restoration of the original crimson color.

Reducing agents, such as zinc and acetic or hydrochloric acid, stannous chloride, sulphurous acid,[2] etc., decolorize solutions of magenta with formation of colorless salts of l e u c a n i l i n e, $C_{20}H_{21}N_3$.   This base differs from the products resulting from the reduction of safranine, magdala-red, and certain other coloring matters, in not being reconverted into rosaniline by atmospheric oxygen.   On the other hand, oxidation of leucaniline to rosaniline can be effected by manganese dioxide, chloranil, and similar agents.

Strong oxidizing agents, such as permanganates, hypochlorites, and chlorine, decolorize solutions of magenta.   Oxidizing agents of moderate power produce new coloring matters, a yellowish-red product known as *aniline-scarlet* being formed by the action of hydrogen peroxide or lead nitrate.   Chromic acid acts on magenta with formation of a brown coloring matter.

Aldehyde and alcoholic solution of shellac convert magenta into blue coloring matters.

Solid magenta dissolves in strong sulphuric acid with yellowish-brown color, becoming violet-red on dilution with water.

DETECTION OF MAGENTA.   When perfectly pure, magenta is not poisonous, but as occurring in commerce it frequently contains arsenic, and hence is unsuitable for coloring confectionery, syrups, wines, etc.   Its use for such purposes is absolutely forbidden in some countries.

[1] A solution of magenta in glacial acetic acid is a delicate reagent for nitrous acid and nitrites, which change the color first to violet, then through blue, green and yellow to orange.   Nitric acid does not show this reaction.

[2] Fuchsine-sulphurous acid, prepared by passing sulphurous actd gas into a dilute solution of magenta until the crimson color has changed to a pale yellow, is a very delicate reagent for aldehydes and some of their derivatives, as these give an intense violet-red color with it.

The detection of magenta is based on the foregoing reactions, but in order to apply these satisfactorily it is usually necessary to isolate the coloring matter more or less perfectly.

For the detection of magenta in *wine* or other colored liquids,[1] about 50 c.c. of the sample should be treated with excess of baryta water, heated to boiling, and filtered. The filtered liquid is then cooled and shaken with ether, which will take up the rosaniline. The ethereal solution, though colorless or nearly so, will communicate a violet-red color to dilute acetic acid, and the resultant solution will exhibit a characteristic absorption-spectrum.[2] On evaporation to dryness, the ethereal solution will yield a residue soluble in strong hydrochloric acid with yellow-brown color, changed to violet-red on dilution, and permanently decolorized by warming with zinc. If a thread of white silk or wool be placed in the ethereal solution, and the ether allowed to evaporate, the rosaniline will be taken up by the fibre, which will acquire a crimson color when moistened with dilute acetic acid. A fairly approximate colorimetric determination of the magenta present may be obtained by comparing the tint with those of standard specimens of wool or silk prepared in a similar manner with known quantities of the coloring matter.

A modification of the above test consists in rendering 50 c.c. of the wine slightly alkaline with ammonia and boiling the liquid with a little white wool till all the alcohol and ammonia are expelled. The wool is then removed, washed with water, and at once heated with a few drops of caustic soda solution till dissolved. After cooling, about 5 c.c. of water and the same measure of alcohol are added, and the liquid is shaken up with 10 c.c. of ether. The ethereal solution is then separated, and examined as already described.

An alternative process for the detection of magenta in wine is to warm 50 c.c. with a strong solution of lead acetate, filter, and add one drop of acetic acid to the filtrate. This is next shaken with 10 c.c. of amylic alcohol, which will remain colorless if the wine be pure, but will be colored red in the presence of *magenta*, red-

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[1] The froth of wine colored with magenta has a distinct violet tint.

[2] In the Paris Municipal Laboratory, where a large number of wines are examined, it is usual to test for *basic* coal-tar dyes, including ordinary magenta, by adding enough baryta water to render the wine slightly alkaline, and then shaking with amylic alcohol or acetic ether. The upper layer, either immediately or after acidulation with acetic acid, will be colored if a basic dye be present.

violet by *archil,* and yellow by *rosolic acid.* If the amylic alcohol be separated and agitated with dilute ammonia, it will be decolorized, the ammoniacal liquid acquiring a bluish-violet color if archil and a red-violet if rosolic acid be present, while magenta communicates no marked color to the ammonia.

Of late years, the use of ordinary magenta for coloring wine has been to a great extent superseded by that of other coal-tar dyes, especially the sulphonated rosaniline known as *acid magenta* To detect this coloring matter, J. H e r z (*Analyst,* xi. 175) recommends that from 30 to 50 c.c of the wine, or preferably 100 c.c. previously concentrated to that volume, should be treated with half its measure of a cold saturated solution of magnesium sulphate, and then from 10 to 20 c.c. of a strong solution of caustic soda stirred in. The precipitate of magnesium hydroxide carries down with it all the natural coloring matter of the wine, and also most of the artificial coloring matters, except archil and sulphonated magenta. If the filtrate be not colorless, or at most merely yellowish-red, the treatment with magnesium sulphate and soda should be repeated. A colorless or yellowish filtrate having been obtained, it is acidulated with dilute sulphuric acid, when if acid magenta or other sulphonated dye be present the liquid will re-acquire its original violet-red color, and from the depth of the tint an approximate estimate of the amount present can be made. If archil be present, the alkaline filtrate will be bluish, becoming litmus-red on addition of acid. If the excess of acid be nearly neutralized, and the colored liquid be shaken for some minutes with peroxide of lead and filtered, a colorless filtrate will be obtained if the previous coloration was due to *archil,* while in the case of the *acid magenta* the red color remains, and its intensity indicates the amount of the dye present.

The gelatinous precipitate of magnesium hydroxide is next stirred up with hot water, and the liquid separated by decantation or filtration.[1] The precipitate is then mixed with sand, dried at

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[1] If only the natural coloring matter of the wine be present, or *bilberry* has been used, this liquid is yellowish-brown ; with *archil,* dark violet ; with *ponceau,* onion or ponceau red; with *cassissine,* pale red or dark yellow; and with *vinicoline bordelaise,* yellowish-red or reddish-brown, giving a violet zone when poured on the surface of strong sulphuric acid. This last coloring matter is said to be a mixture of Biebrich red and elderberry extract. If the colored liquid be agitated with amylic alcohol, and the solution so obtained evaporated, the residue will be dark grey or brownish-grey if only natural or vegetable coloring matters are present; violet in presence of *archil ;* dirty white with either ordinary or acid magenta; dirty yellow-brown with *cassissine ;* and crimson-red with *vinicoline.*

100°, and exhausted with ether. The ethereal solution will contain any ordinary magenta present in the original wine, and can be examined in the manner already described. H e r z mentions a dye called *cassissine* which is extracted together with the ordinary magenta, but dyes wool reddish-brown and is left as a reddish-brown residue on evaporating the ethereal solution. The dyed wool becomes yellow when treated with strong hydrochloric acid, and colorless on adding ammonia.

To detect magenta in wine, R. K a y s e r (*Jour. Soc. Chem Ind.*, iv. 291) recommends that 100 c.c. of the sample should be shaken with 20 c.c. of colorless amylic alcohol. The liquid is then diluted with water and the amylic alcohol layer examined with a spectroscope. If the characteristic absorption-bands of magenta are observed, another portion of the sample should be treated with excess of ammonia, and shaken with amylic alcohol as before, which will be colored red by ordinary magenta, while sulphonated magenta is not extracted from alkaline liquids.[1]

In the Paris Municipal Laboratory, for the detection of *acid dyes* in wine, 10 c.c. of the sample is rendered strongly alkaline by the addition of 2 to 3 c.c. of a 5 per cent. solution of caustic potash; from 2 to 3 c.c. of a 20 per cent. solution of mercuric acetate is next added, and the whole well shaken and filtered. With pure wine, the filtrate is colorless, and remains so even after acidulation

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[1] It is not evident why free rosaniline should color amylic alcohol as stated. There is also a discrepancy between this process and the experience of J. H e r z, who does not appear to have observed the extraction of either ordinary or acid magenta from acid solutions by treatment with amylic alcohol. On the contrary, he finds that the color of the wine after the treatment is cherry-red in the presence of *ordinary magenta*, reddish-violet with *acid magenta*, dark cherry-red with *Bordeaux B;* and yellowish-red with *ponceau RRR*. On evaporating the amylic alcohol solution to dryness and testing the residue with reagents, H e r z observed the following reactions :

COLORING MATTER.	RESIDUE FROM AMYL ALCOHOL.			
	Color.	With Concent. H_2SO_4.	With Concent. HCl.	With Caustic Soda.
Archil.	Violet-red.	Blue.	Red.	Blue.
Bordeaux B.	Carmine.	Carmine.	Carmine.	Carmine.
Ponceau RRR.	Dark-red.	Crimson.	Crimson.	Brown.
Cassissine.	Violet-purple.	Yellow.	Yellowish-brown.	Red.
Vinicoline Bordelaise.	Cherry-red.	Brown.	Red.	Brown.

with hydrochloric acid, but will be yellow or red if acid magenta or other sulphonated coal-tar dye be present.

Further information respecting the detection of foreign coloring matters in wine will be found in vol. i.

The methods already described for the detection of magenta in wine are applicable to other articles colored by it.

The detection of magenta on fibres dyed with it presents no difficulty.   The color is destroyed by sodium sulphide, owing to its reduction to leucaniline.   Alkalies also bleach the color from liberation of rosaniline, which may be extracted by ether.   Strong hydrochloric acid turns the fabric yellow or brown, the color being restored by copious dilution.

L i e b m a n n and S t u d e r (*Jour. Soc. Chem. Ind.*, v. 288) recommend that 100 c.c. of the wine should be evaporated to about 10 c.c., saturated with sulphur dioxide, and then precipitated with lead acetate.   To the filtered liquid a drop of aldehyde or acetone is added, when a violet coloration will be produced if magenta or acid magenta be present even in the proportion of one milligramme per litre.   The test is equally applicable to syrups, lozenges, etc. The treatment with lead acetate is not essential.   A similar method may be employed for the detection of magenta in cudbear and archil.

In testing wine for magenta it should always be borne in mind that the coloring matter is precipitated by tannin, and hence is often present most largely in the deposit, from which it may be extracted by treatment with an alkali and agitation with ether.

EXAMINATION OF COMMERCIAL MAGENTA.   Pure magenta consists simply of the hydrochloride or other salt of rosaniline, mixed with more or less of the corresponding compound of pararosaniline. The commercial product generally contains, in addition, more or less water, mineral impurities, resinous substances, and, if prepared by the arsenic acid process, a notable quantity of arsenic. Besides these impurities, actual adulterants are sometimes present, the most usual being sugar, starch, dextrin, sodium sulphate, and occasionally bronze powder.

Magenta of good quality being generally well crystallized, powdered or imperfectly crystalline specimens are aways open to suspicion.

The blue shades of magenta are generally the purest.   The yellow shades, if made by the arsenic acid process, usually contain *phosphine;* magenta made by the nitrobenzene process contains no phosphine.

A solution of pure magenta is entirely decolorized by sulphurous acid, while impure samples are turned yellow or brown; or the hot aqueous solution of the sample may be treated with hydrochloric acid, and zinc-dust then gradually added in small quantities at a time, till the red color is destroyed. With pure magenta the reduced liquid will be colorless, but if *chrysaniline* be present it will have a yellow tint.

Arsenic is sometimes present in commercial magenta in considerable proportion, as much as $6\frac{1}{2}$ per cent. having been met with. It may be detected by Marsh's test. For its determination, the acidulated solution may be treated with bromine water, excess of ammonia added, the liquid filtered if necessary, and magnesia mixture then added. A precipitate of the ammonio-magnesium arseniate, deposited in streaks in the track of the glass rod used for stirring, will be gradually formed if arsenic be present, The arseniate may be distinguished from the similar phosphate by washing the precipitate or streaks with water, and adding silver nitrate, when the arsenite will be turned brown, or the phosphate yellow.

The detection of other impurities and adulterants of magenta will be described in the section on the "Examination of Commercial Coloring Matters."

ACID MAGENTA, called also *magenta S* and *rubine S*,[1] is obtained by heating ordinary magenta with fuming sulphuric acid or sulphonic chloride, SO_3HCl. The product is poured into water, neutralized with milk of lime, the solution filtered from the calcium sulphate, and the filtrate decomposed by sodium carbonate. The calcium carbonate is filtered off and the filtrate evaporated to dryness. Acid magenta occurs in grains or powder of a green color and metallic lustre. It dissolves readily in water, forming a bluish-red solution, which is nearly decolorized by alkalies without a precipitate being formed, and nothing is yielded to ether. Dilute acids, even carbonic acid, restore the color, which is not materially altered by a considerable excess. In strong sulphuric acid, the solid dye dissolves with yellow color, becoming gradually red on dilution.

According to C. Blarez, all red coal-tar dyes except acid magenta, and also all red vegetable coloring matters, are completely decolorized when their aqueous solutions are slightly acidulated with tartaric acid and digested with dioxide of lead.

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[1] Impure forms of acid magenta are to be met with under the names of *Maroon S*, *Grenat S*, *Acid Cerise*, *Cardinal Red S*, *Acid Maroon*, etc.

In its behavior with reducing agents and acetone, acid magenta reacts like the basic dye.

Acid magenta is employed for coloring red wines. Being insoluble in ether, either in acid or alkaline liquids, it may be distinguished from ordinary magenta, and may be more definitely recognized as described on page 282.[1]

Acid magenta has only about half the dyeing power of ordinary magenta, but can be dyed from strongly acid baths, and hence is conveniently employed in conjunction with acid yellow, indigo-carmine, etc.

On the fibre, acid magenta is unaffected in color by a mixture of equal measures of hydrochloric acid and water, whereas ordinary magenta is turned yellow or brown. The reagent dissolves some of the acid magenta, and acquires a cherry-red color.

Aniline Blues.

As stated already (page 272) the phenylated derivatives of rosaniline and pararosaniline dye bluer shades than the unsubstituted bases, and this in proportion to the number of hydrogen atoms replaced by p h e n y l, C_6H_5. Thus the coloring matter known as *regina violet* is chiefly a salt of diphenyl-rosaniline, while the various commercial aniline blues are mostly triphenylated derivatives; and Benedikt states that hexaphenyl-rosaniline yields a purer blue than any other coloring matter known.

Besides a few aniline colors of a somewhat different constitution, there occur in commerce two parallel series of blue dyes, which are triphenylated derivatives of pararosaniline and rosaniline respectively. Thus:—

	Triphenyl-para-rosaniline. $C\begin{cases}C_6H_4.NH(C_6H_5)\\C_6H_4.NH(C_6H_5)\\C_6H_4.NH(C_6H_5)\\OH\end{cases}$	Triphenyl-rosaniline. $C\begin{cases}C_6H_3(CH_3).NH(C_6H_5)\\C_6H_4.NH(C_6H_5)\\C_6H_4.NH(C_6H_5)\\OH\end{cases}$
Hydrochloride.	Diphenylamine blue. Pararosaniline blue.	Rosaniline blue. Aniline blue. Spirit blue. Paris blue.
Sodium monosulphonate.	Alkali blue D. Soluble Diphenylamine blue.	Alkali blue. Soluble blue. Nicholson's blue.
Sodium disulphonate.	Bavarian blue DSF.	Silk blue.
Sodium trisulphonate.	Methyl blue BI for cotton. Bavarian blue DEF.	Soluble blue. China blue. Cotton blue. Opal blue. Water blue O or 6 B extra.

[1] Magenta may also be distinguished from acid magenta by treatment with sulphurous acid, when the rosaniline salt will be decolorized, but will assume a violet

The parallel compounds from para-rosaniline and rosaniline present a close analytical and general resemblance. In addition, the phenylated products from commercial rosaniline invariably contain more or less of their lower homologues (from para-rosaniline), and hence there is no sharp distinction between the two series of dyes.

Diphenylamine Blue or Para-rosaniline Blue[1] is the hydrochloride of triphenyl-pararosaniline, and contains $C_{19}H_{14}(C_6H_3)_3N_3 \cdot HCl$. It is prepared by heating d i p h e n y l a m i n e, $(C_6H_5)_2 : NH$, to 120°–130° with oxalic acid. The excess of oxalic acid is removed by washing with water, and unaltered diphenylamine by boiling with benzene, the residue being then converted into the hydrochloride. The commercial dye forms a brownish powder, having an odor resembling that of diphenylamine. It is insoluble in water and only sparingly soluble in cold alcohol, but dissolves more readily on heating. The solution is turned greenish by hydrochloric acid. A two per cent. solution of the coloring matter in methylated spirit is employed to produce light and very pure shades of blue on silk. Diphenylamine blue dissolves in strong sulphuric acid with brownish-yellow color, a blue precipitate being produced on dilution.

The coloring matter known as *azuline* or *azurine* is an impure hydrochloride of triphenyl-pararosaniline.

Coloring matters known as *methyl blue*[2] and *ethyl blue* are obtainable by the action of methyl or ethyl chloride on diphenylamine blue; or by heating methyl- or ethyl-diphenylamine with oxalic acid. The products dye silk a still purer blue than that produced by diphenylamine blue. One of the purest blues is obtained by treating methyl-diphenylamine at 100° with c h l o r a n i l (tetrachlorquinone), $C_6Cl_4O_2$,[3] and then further heating to 130°. The product is reduced to powder, washed with hydrochloric acid, dissolved in alcohol, and precipitated by water.

coloration with an alcoholic solution of form- or acetaldehyde. Acid magenta subjected to the same treatment assumes a rose tint of the original color. Magenta is also soluble in amyl alcohol in the presence an alkali, whereas acid magenta is not.

[1] Also known as *Bavarian Blue* spirit soluble.

[2] Also known as *Methyl Blue MBI, Brilliant Cotton Blue, XL Soluble Blue, Methyl Water Blue, Cotton Blue, Bavarian Blue DBF, Soluble Blue 8B, 10B, Pure Blue BSI.*

[3] Prepared by the action of potassium chlorate and hydrochloric acid on phenol.

Rosaniline Blue, also called *Spirit Blue, Aniline Blue, Opal Blue, Gentian Blue 6 B, Fine Blue, Hessian Blue,* is a salt of t r i p h e n y l- r o s a n i l i n e, containing more or less of the corresponding salt of triphenyl-pararosaniline. To prepare it, rosaniline (prepared by precipitating a solution of the purest bluish magenta with ammonia or lime) is heated to about 180° with ten times its weight of aniline and some benzoic acid. The excess of aniline, together with the ammonia formed in the reaction, distils over. The product is neutralized with dilute hydrochloric acid, when aniline hydrochloride dissolves and the salt of the new base remains insoluble. This is washed first with dilute hydrochloric acid and then with water, and dried and powdered.[1]

The most usual form of occurrence of triphenylrosaniline is as the h y d r o c h l o r i d e, $C_{20}H_{16}(C_6H_5)_3N_3.HCl$, but the s u l p h a t e and a c e t a t e are also met with. The first salt forms a greyish-green or brownish powder, which becomes pure blue at 100°; the sulphate and acetate bluish-violet, lustreless powders. In cold water, the salts of triphenylrosaniline are quite insoluble, and nearly so in hot. In alcohol the acetate dissolves easily, and the hydrochloride and sulphate with more difficulty, to form deep blue solutions, unchanged or turned greenish by hydrochloric acid, and in which stannous chloride produces a blue precipitate. A cold alcoholic solution of spirit blue becomes brownish-red with soda or ammonia, but at a boiling heat a colorless solution is produced, and on dilution with water this yields a white precipitate of free triphenylrosaniline, $C_{20}H_{17}(C_6H_5)_3N_3.OH$, which rapidly becomes blue in the air. In concentrated sulphuric acid, spirit blue dissolves with brownish-yellow color, and on dilution with water a blue precipitate is produced.

Spirit blue is employed to produce bright blues on wool. The articles are dyed in a bath containing alum, sulphuric acid, or stannic chloride. Fibres dyed with spirit blue are nearly decolor-

[1] The blue obtained from rosaniline, as described in the text, is of a lower price and quality than diphenylamine blue. The less pure products have a reddish shade, especially observable in artificial light. The best qualities appear pure blue by gas or lamp light, and are sometimes known as *bleu de nuit* and *bleu lumière*, but must not be confused with the *night blue* described on another page. These qualities are also known as *spirit-blue 5 B* and *6 B*, the redder shades being described as *2 B, 3 B*, etc., according to their quality. Spirit-blue is sometimes further purified by dissolving it in aniline and precipitating by hydrochloric acid, and by other methods. Such purified products are known as *opal blue* or *basic blue*.

ized by hydrochloric acid, turned greyish-violet by soda, and changed to light blue, fading to colorless, by ammonia. Alcohol strips the fibre even in the cold.

SULPHONATED ANILINE BLUES.

Diphenylamine blue and spirit blue being insoluble in water, their practical application is attended with some inconvenience, to obviate which they are frequently s u l p h o n a t e d, with production of soluble coloring matters known as *Soluble Blue, Water Blue, Water Blue 6 B, China Blue, London Blue, Cotton Blue, Opal Blue, Marine Blue.*[1]

The greater the number of SO_3H groups that are introduced into triphenylrosaniline or its homologues, the more readily soluble the products become, but their fastness to light and air, soap, and alkalies decreases in the same proportion. Hence the higher sulphonic acids, such as triphenyl-rosaniline tetrasulphonic acid, are never prepared.

The sulphonated aniline blues are prepared by heating diphenylamine blue and spirit blue with concentrated sulphuric acid, the extent of the sulphonation depending on the proportion of acid used and the temperature employed. A soluble diphenylamine blue may be prepared directly by heating diphenylamine-sulphonic acid with oxalic acid, instead of sulphonating the previously prepared triphenylpararosaniline.

TRIPHENYLROSANILINE - MONOSULPHONIC ACID has the formula $C_{20}H_{15}(SO_3H)(C_6H_5)_3N_3$, and is formed by dissolving spirit blue in strong sulphuric acid and heating the solution to 30°–35° C. for five or six hours. On pouring the resultant brownish-yellow solution into water, the sulphonic acid is obtained as a bulky blue precipitate, which after being dried at 100° forms small grains having a metallic lustre. Its alkali-metal salts are soluble in water, but those formed with the heavy metals and alkaline-earth metals are insoluble or nearly so. By digesting the washed sulphonic acid in a quantity of caustic soda solution somewhat less than that required to combine with it, and filtering, a solution of the s o d i u m s a l t is obtained, from which the solid compound may be prepared by saturating the liquid with common salt, or evaporating it to dryness with addition of a little ammonium carbonate.

Sodium triphenylrosaniline-monosulphonate forms the commercial

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[1] Also known as *Cotton Blue 3 B, Bleu de Lyon, Water Blue B, BS, Blue B VSI, Blackley Blue, Pure Blue, Water Blue OO.*

dye-stuff known as *Nicholson's Blue*, *Alkali Blue*, *Soluble Blue* or *Fast Blue*. It occurs in lumps or powder of a greyish, brownish, or dull blue color. It dissolves readily in hot water, with light brown or bluish color, which becomes deep blue on adding acetic acid, and on boiling the acidulated liquid the free sulphonic acid separates as a blue precipitate. Hydrochloric acid produces the same reaction in the cold, and on filtering a colorless liquid is obtained, unless a di- or trisulphonate be present. Caustic soda turns the solution of soluble blue reddish-violet, the color changing on boiling to reddish-brown. Excess of ammonia decolorizes the solution. Calcium chloride and stannous chloride produce blue precipitates. Soluble blue dissolves in strong sulphuric acid with fine brownish-red color, becoming blue on dilution with water.

If wool be immersed in a hot solution of alkali blue, preferably containing borax, sodium silicate, sodium carbonate, or ammonia, the nearly colorless salt is taken up by the fibre and cannot be removed by washing with water; but on subsequently immersing the fibre in dilute sulphuric acid the blue color is developed.

Cold alcohol readily removes the color from wool or silk dyed with alkali blue. Caustic soda turns the fibre a yellowish-brown, while ammonia immediately destroys the color. Hydrochloric acid nearly decolorizes the fibre, and an acid solution of stannous chloride destroys it gradually.

Commercial alkali blue is liable to contain various impurities and adulterations. It should dissolve without residue in about five parts of hot water. Sugar, starch, and dextrin are sometimes added, and a considerable proportion of sodium carbonate, sulphate, or chloride is often present. Arsenic is not an unusual contamination. Alcohol dissolves the dye and leaves sodium sulphate and carbonate insoluble. The dye may be precipitated by saturating the aqueous solution with purified common salt, while sodium carbonate and sulphate remain in solution. The sulphate of sodium contained in the residue left on ignition represents that formed from the sulphonate, as well as that pre-existing as sulphate. Pure sodium triphenylrosaniline-monosulphonate will yield 22.6 per cent. of Na_2SO_4 on fusion with sodium carbonate and nitre. On ignition alone a low result is obtained, the sodium present being insufficient to fix all the sulphur, besides which more or less sulphide and sulphite will probably be formed.

Sodium triphenylpararosaniline-monosulphonate is known in com-

merce as *Alkali Blue D.*[1] In its reactions it closely resembles its homologue from rosaniline, but is nearly insoluble in cold water. and in hot water forms a blue solution which has an odor of diphenylamine.

TRIPHENYLROSANILINE-DISULPHONIC ACID, having the formula $C_{20}H_{14}(SO_3H)_2(C_6H_5)_3N_3$, is obtained, together with the trisulphonic acid, when triphenylrosaniline hydrochloride (spirit blue) is digested with 4 or 5 parts strong sulphuric acid at 60° C. for five or six hours, and the temperature finally increased to 100°–110°. If the product be diluted with three or four times the quantity of water, both sulphonic acids are precipitated, but if a comparatively large quantity of water be used the precipitate consists mainly of the disulphonic acid, while the trisulphonic acid dissolves and may be obtained as a blue precipitate by treating the filtrate with common salt or hydrochloric acid in excess. Triphenylrosaniline-disulphonic acid is slightly soluble in water, but insoluble in acid liquids, and hence is thrown down as as a blue precipitate on acidulating the solution of one of its salts. Excess of soda turns the solution of its salts yellow. The s o d i u m s a l t occurs in commerce under the name of *Silk Blue*, and *Bavarian Blue DSF, Methyl Blue for Silk MLB, Marine Blue B*, consists principally of the corresponding derivative of pararosaniline, while *Blackley Blue* is the sodium salt of diphenyl-tolyl-rosaniline-sulphonic acid.

TRIPHENYLROSANILINE-TRISULPHONIC ACID, of the composition $C_{20}H_{13}(SO_3Na)_3(C_6H_5)_3N_3$, is obtained as indicated above. It is soluble in water and alcohol. The *sodium, ammonium*, and *calcium salts*, mixed with more or less of the corresponding disulphonates, form the commercial coloring matters known as *Water Blue, Cotton Blue*, etc. (page 287). The a m m o n i u m s a l t forms dark lumps or grains having a coppery lustre; the s o d i u m s a l t usually occurs as dark blue irregular lumps. *China Blue* is a very porous variety of water blue, obtained by adding carbonate of ammonium to a very concentrated and slightly acid solution of the coloring matter.

Water blue is more soluble than alkali blue, and crystallizes from its concentrated hot solution in flakes having a metallic lustre. Its solution is not completely precipitated by hydrochloric acid, under any circumstances; and not at all unless a large excess of the reagent be used or d i s u l p h o n a t e be present. Caustic soda decolorizes the solution or turns it reddish-brown. Water

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[1] Also known as *Methyl Alkali Blue* and *Alkali Blue 6 B.*

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blue dissolves in strong sulphuric acid with dark yellowish-red color, and on dilution a blue solution is formed, sometimes accompanied by partial precipitation.

Water blue differs from alkali blue in not being taken up by wool from an alkaline solution, and hence the fibre so treated is not rendered blue by subsequent immersion in dilute acid.

Strong sulphuric acid dissolves water blue from fibres dyed with it, with a blue coloration, and a hydrochloric acid solution of stannous chloride behaves similarly. Caustic soda turns the fibre reddish-brown, and ammonia decolorizes it immediately. Alcohol has no effect on the dyed fibre, even when boiling.

Water blue is chiefly used for dyeing cotton, being fixed by means of tannin, or by alizarin oil, in conjunction with aluminium, antimony, or tin compounds. It is dyed on silk and wool in an acid bath, and in this case is always used in conjunction with other coloring matters.

The coloring matters known as *Bavarian Blue DBF, Methyl-Blue M, BI for cotton*, etc., chiefly consist of the sodium salt of *tri phenyl-pararosaniline-trisulphonic acid*, and closely resemble the homologue, ordinary water blue.

BLUES FROM TETRAMETHYL-DIAMIDO-BENZOPHENONE.

Several interesting coloring matters are obtainable by the reaction of tetramethyl-diamido-benzophenone on phenyl-alphanaphthylamine and its homologues in presence of condensing agents. Although the mode of preparation of these dyes is entirely different from that of diphenylamine blue and rosaniline blue, the products bear a certain constitutional relationship to these products.

Victoria and night blues dye wool and silk in a bath acidulated with acetic acid. Cotton is first mordanted with alizarin oil and aluminium acetate. Sulphuric acid changes the color of the fibre to orange or reddish-brown, but the original blue color is restored by washing.

Victoria Blue B or BS is the hydrochloride of tetramethyl-phenyl-triamido-*a*-naphthyl-diphenylcarbinol, and is prepared by the action of phenyl-*a*-naphthylamine on tetramethyl-diamido-benzophenone chloride. It is sparingly soluble in cold, but readily so in hot water, yielding a blue solution which gradually deposits a reddish resinous precipitate of free base on boiling. This decomposition is prevented by the addition of acetic acid. In the presence of mineral acids the dyestuff is less soluble than in pure water. When dyed on wool Victoria Blue is very liable

to rub; this fault may be avoided by boiling the wool with aluminium sulphate before dyeing.

Victoria Blue 4 R is the hydrochloride of pentamethyl-phenyl-triamido-a-naphthyl-diphenylcarbinol. It is made in a manner analogous to the preceding dyestuff, which it greatly resembles in its general properties, with the exception that it dyes a redder shade.

Night Blue is the hydrochloride of tetramethyl-tolyl-triamido-a-naphthyl-diphenylcarbinol. Its preparation is analogous to the preceding blues. It is soluble in water with a fine blue color which becomes turbid and is precipitated by boiling. Its solubility is increased by the addition of acetic acid. From the fact that night blue is completely precipitated from its solution by many other dyestuffs such as picric acid, naphthol yellow, etc., it is used as a reagent for the quantitative estimation of such dyestuffs (see p. 117).

Aniline Violets.

By the substitution, partial or complete, of the hydrogen of the NH_2 groups of rosaniline and pararosaniline by methyl or ethyl, various violet coloring matters are obtained, those compounds in which the substitution is carried furthest yielding the bluest shades. These methylated and ethylated rosanilines (and para-rosanilines) with a few compounds in which a molecule of phenyl, tolyl, or benzyl is introduced, constitute the *aniline violets* of commerce.

The aniline violets are usually greenish powders or crystals with metallic reflection, soluble in water to fine violet solutions which dye silk and wool violet without a mordant. They can be fixed on cotton by tannin and tartar-emetic. The aniline violets are decolorized by boiling with potassium cyanide, a turbid solution being produced. With sulphuric acid they dissolve with yellow or brownish-yellow color, and present a very close analytical resemblance, as will be seen in the annexed tables of their physical characters and chemical reactions.

Methyl Violet B, METHYL-ANILINE VIOLET, PARIS VIOLET, DAHLIA, DIRECT VIOLET, METHYL VIOLET 2B, or METHYL VIOLET V3 (page 273), is the hydrochloride or double zinc salt of pentamethyl-pararosaniline. It is produced by the direct oxidation of dimethylaniline (from dimethyl-toluidine) by cupric chloride:[1]—

$$3C_6H_5 . N(CH_3)_2 + 3O = 3H_2O + C_{19}H_{12}(CH_3)_5N_3.$$
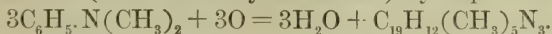
[1] Sulphate of copper is treated in solution with a large excess of common salt,

A coloring matter known as *chloranil-violet*, probably identical with methyl-violet, is obtained by the reaction of dimethylaniline and chloranil (tetrachlorquinone).

Methyl-aniline violet occurs in commerce as a hydrochloride, and also a compound of this salt with zinc chloride. The h y d r o - c h l o r i d e forms small crystals, the z i n c d o u b l e s a l t a powder or irregular lumps. Both varieties of the coloring matter exhibit a green metallic reflection, and are easily soluble in water, alcohol, amyl alcohol, and chloroform.

Dilute solutions of methyl violet are turned pure blue by a very small addition of hydrochloric acid. With more acid they appear green in thin layers, but red and somewhat turbid in thicker strata. Excess of acid turns the solution red or yellowish-brown from the formation of an acid salt. Ammonia produces a lilac and caustic soda a violet-brown precipitate, the solution becoming colorless on boiling.

With chromic acid methyl-violet gives a dirty violet and with stannous chloride a blue-violet precipitate, becoming lighter on boiling. Hypochlorites decolorize solutions of methyl violet.

Methyl violet is completely precipitated by soluble ferrocyanides and ferricyanides, and hence may be conveniently fixed on cotton mordanted with potassium ferrocyanide, or in the fibres of which zinc ferrocyanide has been previously deposited by double decomposition. In this manner methyl violet may be used for printing calico. It is also fixed by albumin or tannin, and is used for topping goods dyed with iron mordants and alizarin, in order to brighten the fast violet thus produced.

Boiling with water gradually decolorizes fibres dyed with methyl violet. Hydrochloric acid removes part of the color and the fibre becomes greenish-yellow, but the original color is restored on washing with water. Ammonia decolorizes the fibre. Caustic soda turns it reddish-violet and gradually decolorizes it. Treated with a hydrochloric acid solution of stannous chloride, the fibre becomes a yellow or greenish-yellow color.

Methyl violet is liable to much the same adulterations as other

and acetic acid and dimethylaniline added. The product is moulded into cakes which are dried at 40° to 50° C. These are treated with a quantity of boiling water insufficient to dissolve all the common salt. The aniline violet, being insoluble in strong brine, remains as a residue. It is dissolved in water, the copper removed by sulphuretted hydrogen, and the coloring matter precipitated by treating the filtrate with common salt. It is again purified by re-solution and crystallization or salting out, or is converted into the zinc double salt.

aniline dyes. It may be determined volumetrically by precipitation with picric acid (page 118), the formula of the p i c r a t e being $C_{24}H_{27}N_3.C_6H_2(NO_2)_3OH$.

Crystal Violet, VIOLET C, CRYSTAL VIOLET 5 BO, or CRYSTAL VIOLET O is the hydrochloride of h e x a m e t h y l - p a r a r o s a n i - l i n e. It is obtained by the reaction of tetra-methyl-diamido-benzophenone chloride or carbon oxychloride on dimethyl-aniline, the reaction in the latter case being:—

$$[C_6H_5.N(CH_3)_2]_3 + 2COCl_2 = Cl.C[C_6H_4.N(CH_3)_2]_3 + 3HCl + CO_2.$$
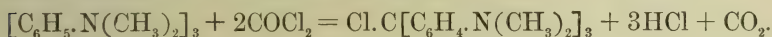
Crystal violet forms long hexagonal prisms or pyramids. The crystals have a beetle-green reflection if anhydrous, but a variety containing 8 *aqua* also occurs, the reflection from which is bronze. When heated to 100°, the crystals become brown and suffer slight decomposition. Crystal violet is soluble both in water and alcohol, but crystallizes more readily from the former than the latter menstruum. The solutions are deep violet-blue, and dye wool and silk a very blue shade of violet. On cotton, crystal violet is fixed by tannin and tartar-emetic.

According to G. Z e t t e r, crystal violet dissolves in strong sulphuric acid with orange color, which is unchanged on dilution; but according to other observers the solution in sulphuric acid is yellow, changing on dilution to green, blue and violet.

On adding platinic chloride to a solution of crystal violet in strong hydrochloric acid, the c h l o r o p l a t i n a t e is obtained as a brick-red precipitate of the composition $[C_{19}H_{12}(CH_3)_6N_3Cl]_4$ $(PtCl_4)_3$.

On heating crystal violet in a closed tube to 120° C. with an aqueous solution of ammonium sulphide, a l e u c o - b a s e is formed of the formula $C_{25}H_{21}N_3$, which melts at 173° after being purified by crystallization from alcohol.

Crystal violet forms a very insoluble p i c r a t e, a fact which may be utilized for its determination and assay (see page 118).

Benzyl Violet [1] is prepared by heating methyl violet with benzyl chloride, $C_6H_5.CH_2Cl$, alcohol, and lime or soda, in an apparatus furnished with a reflux condenser. A series of products are thus formed, becoming bluer the greater the number of benzyl atoms introduced into the molecule. The commercial product is the hydrochloride of zinc double salt. Benzyl violet

[1] Also known as *Paris Violet 6 B, 7 B, Methyl Violet 6 B, 7 B, Violet 5 B, 6 B,* or *7 B.*

closely resembles methyl violet, but dyes somewhat bluer shades. Fibres dyed by benzyl violet are turned light blue by caustic soda; but if dyed by methyl violet red-violet. In both cases, the material is decolorized after a time.

Hofmann's Violets [1] are of historical interest, being, with the exception of *mauve* (page 100), the first aniline violets produced, but they have now been nearly superseded by the newer colors, such as methyl violet. They are produced by acting on an alcoholic solution of rosaniline with caustic soda and iodide of methyl or ethyl. The larger the proportion of alkyl iodide employed, the greater is the substitution and the bluer the product. The ethylated rosanilines are redder than the corresponding methyl-derivatives.

Regina Purple (Regina Violet, Imperial Violet, or Phenyl Violet) is probably a mixture of the acetates of phenyl- and orthotolyl-rosaniline together with the same salts of pararosaniline. It is obtained from the "échappés" formed in the manufacture of magenta. Parma Violet or Regina Violet spirit-soluble is a similar product supposed to be the hydrochloride of diphenylrosaniline, and is a bye-product from magenta made after the nitrobenzene method. Neither of these violets is used to any extent at the present time, and they are fast becoming obsolete.

Acid Violets. There are several of these dyestuffs, which in general resemble acid magenta, but give a bluer shade in dyeing. For the most part they are sodium salts of the sulphonic acids of methyl- and ethyl-rosaniline and pararosaniline. The shades are usually quite fast to light and resist milling fairly well, but are destroyed by alkalies. Among these violets are to be found Red Violet 4RS, [2] and 5RS, which are the sodium trisulphonates of dimethylrosaniline and ethylrosaniline respectively; Acid Violet 6B [3] or Acid Violet 4 B N is the sodium sulphonate of benzyl-pentamethylpararosaniline.

Formyl Violet S 4 B [4] is also a rosaniline violet which is

[1] Also known as *Iodine Violet*, *Red Violet 5 R extra*, *Violet 4 RN*, *Violet R*, *RR*, *5 R*, *Dahlia*, and *Primula*.

[2] Also called Acid Violet 4RS.

[3] There is also an Acid Violet 6 B made by the Berlin Aniline Works which is the sodium sulphonate of dimethyl-dibenzyl-diethyl-triamidotriphenyl carbinol. Acid violet 4BN is also known as Acid Violet 7B and Acid Violet N. Wool Blue S is a mixture of acid violet 4BN with a light green.

[4] Also known as Acid Violet 4 B extra, Acid Violet 6 B (of Geigy).

obtained by the condensation of diethyldibenzyldiamido-diphenyl-methane disulphonic acid with diethylaniline. It gives a bluer shade than acid magenta and resembles the acid violets very closely.

Acid violets of a red shade which have been made by the alky-lation of acid magenta, usually contain some excess of the latter. In order to effect a separation of the magenta from the acid violet the coloring matter is dissolved in hot water and precipitated with basic lead acetate. This precipitate is decomposed by ammonium carbonate, and filtered; the coloring matter in the filtrate being estimated by evaporation and weighing of the residue. The washings are acidulated with sulphuric acid, then made alkaline with lime, and filtered. The filtrate is evaporated to dryness and treated with alcohol, which extracts the lime salts of the violet coloring matters, leaving that of the acid magenta undissolved. The shade of the precipitate and the two portions of the washings can be ascertained by dye trials.

Aniline Greens.

The green coloring matters derived from triphenylmethane may be divided into two classes, one of which is represented by *methyl green* and the other by *benzaldehyde green*. The former dyes are derivatives of triamido-triphenylmethane, while the latter are derived from diamido-triphenylmethane. The sulphonated aniline greens which are found in commerce are mostly dyes of the latter series.

METHYL-GREEN or METHYLANILINE GREEN[1] is the most import-ant of the basic green dyes of Class I. (page 273). It is prepared by acting on pentamethyl-pararosaniline (the base of methyl violet) by methyl chloride, in amylic alcohol solution, and con-verting the product into the double zinc salt.

Methylaniline green is the double salt with zinc chloride of the hydrochloride of chlormethyl-hexamethyl-pararosaniline,[2] and has the formula:—$C_{19}H_{12}(CH_3)_6N_3.Cl.CH_3Cl + ZnCl_2 + H_2O$. It occurs in commerce either in small green needles, in large coppery prisms, or as a light green powder. It dissolves readily with bluish-green color in water and alcohol, but is soluble in amyl alcohol. This last character distinguishes methyl green (and

[1] Also known as *Paris Green, Light Green, Double Green* and *Green Powder.*

[2] This base may be conveniently referred to as "verdaniline."

probably the other greens of Class I.) from benzaldehyde green
(and its allies). Methylaniline green is insoluble in ether or
benzene, and may be precipitated from its alcoholic solution by
addition of ether.

Dilute acids color the solution to greenish-yellow, a tri-acid salt
being formed, but on dilution with water the original color is
restored. Hypochlorites destroy the color of methyl green, and
stannous chloride and other reducing agents gradually decolor-
ize it.

On adding a strong solution of caustic soda to one of methyl
green a resinous precipitate is produced. This precipitate is the
f r e e   b a s e, and contains $C_{19}H_{12}(CH_3)_6N_3.OH.CH_3Cl$. It is
soluble in pure water, and on treatment with moist oxide of
silver yields silver chloride and the non-chlorinated b a s e,
$C_{19}H_{12}(CH_3)_6N_3.OH.CH_3.OH$, is produced.

As might be expected from its constitution and mode of forma-
tion, methyl green readily splits up into methyl chloride and
methyl violet. The decomposition occurs gradually at 100°, and
rapidly at 120°–130° C. Hence if filter-paper be moistened with
a solution of methyl green, and then strongly dried, it will acquire
a violet color. This reaction, which is equally applicable to fibres
dyed with the coloring matter, is characteristic of methyl green
and its immediate allies (e. g., ethyl green, iodine green).

The adulterations and impurities of methyl green and other
aniline greens are described on page 300.

Methyl green is now rarely used for dyeing wool. When it is,
sulphur or zinc sulphide is one of the best mordants. Silk is
dyed in a warm bath, to which picric, tartaric, or acetic acid is
sometimes added. On cotton, methyl green is fixed by means of
tannin.

On the fibre, methyl green may be recognized by the change of
color on heating strongly. Excess of hydrochloric acid turns the
fibre yellow, but the original color is restored by washing. The
dye is removed by alcohol or acetic acid, the liquid being colored
bluish-green. Alkalies and reducing agents decolorize the fibre.

IODINE GREEN[1] presents the closest resemblance to methyl green,
with which it is homologous. As formerly prepared, with methyl
iodide, it gave off violet vapors of iodine when heated with strong
sulphuric acid, but as at present manufactured, by the treatment

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[1] Also known as *Night Green* and *Pomona Green.*

of rosaniline with methyl chloride, the dye does not give this reaction.

Perkin's green resembles iodine green, but is precipitated by sodium carbonate in the cold.

SPIRIT-SOLUBLE GREEN is obtained as an insoluble crystalline p**i**crate by adding picric acid to a solution of iodine-green (or methyl-green?). It occurred in commerce as a dark green paste, nearly insoluble in water but dissolving in alcohol. At present it is obsolete.

Malachite Green, or BENZALDEHYDE GREEN,[1] is obtained by the reaction of dimethyl-aniline on benzaldehyde, whereby tetramethyl-paradiamido-triphenyl-methane is produced, thus:—

$$C_6H_5.COH + 2C_6H_5N(CH_3)_2 = H_2O + H.C(C_6H_5)[C_6H_4N(CH_3)_2]_2.$$

The hydrochloric acid solution of the product is oxidized by peroxide of lead at 60°–80° C., preferably with addition of a little chloranil. The lead is removed by sodium sulphate, and the filtrate treated with common salt and zinc chloride, when the double zinc compound is precipitated.

The *double zinc chloride* of tetramethyl-diamido-triphenyl-carbinol contains $3C_{23}H_{24}N_2, HCl + 2ZnCl_2 + 2H_2O$. It forms brass-yellow prisms, with a yellowish-green reflection.

The *double iron chloride* (ferrous) also occurs in commerce as an inferior quality of benzaldehyde green.

The *oxalate,* $C_{23}H_{24}N_2, H_2C_2O_4$, forms scales having a green metallic reflection.

All the commercial forms of benzaldehyde green dissolve easily in water and alcohol. They are also soluble in amylic alcohol, which character distinguishes them from methyl green (and its allies).

The *free base* of benzaldehyde green is obtained as a green precipitate on adding an alkali to the solution of one of its salts. The precipitate is soluble in ether and petroleum spirit, and after crystallization from the latter solvent forms colorless needles, which melt at 126°–130° C.

The base of malachite green combines with both one and two molecules of picric acid to form insoluble picrates.

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[1] Also known as *Malachite Green B, Benzal Green, New Victoria Green, New Green, Solid Green, Solid Green O, Diamond Green, Dragon Green, Benzoyl Green* and *Fast Green.*

The solutions of benzaldehyde green are bluish-green. By concentrated hydrochloric acid they are changed to orange-yellow, but the green color is restored by dilution. Hypochlorites decolorize the solution, and stannous chloride forms a green precipitate.

Benzaldehyde green may be detected on fibres dyed with it by the orange coloration with hydrochloric acid, restored to green by washing, and by the decolorization produced by ammonia, soda, or soap. From methyl green it is distinguished by not turning violet when heated.

Ethyl Green (Brilliant Green, Malachite Green G, New Victoria Green, Emerald Green, Fast Green J, Diamond Green G, Smaragdgreen, and Solid Green J, J J O) is homologous with Malachite Green, and consists either of the sulphate or zinc chloride compound of tetraethyl-diamido-triphenyl-carbinol. It is prepared in a manner similar to that of malachite green, diethylaniline being substituted for the dimethylaniline. The dyeing power of brilliant green is not so intense as that of malachite green, and its shade is yellower.

Victoria Green 3 B (New Fast Green 3 B, and New Solid Green B B), is a chlorinated malachite green, being obtained from dichlorbenzaldehyde and dimethylaniline. It occurs as the hydrochloride (or zinc chloride compound) of tetra-methyl-diamido-dichlor-triphenylcarbinol. In its general properties it is about the same as malachite green, but it dyes a bluer shade than the latter.

HELVETIA GREEN (Acid Green) is the type of the sulphonated aniline greens, the reactions of which have already been described. It differs from benzaldehyde green by giving no precipitate with caustic soda in dilute solutions, though strong soda solution produces a white precipitate. On the fibre, acid green closely simulates benzaldehyde green, but is turned greenish-yellow by hydrochloric acid, the liquid itself becoming yellow; whereas fibres dyed with benzaldehyde green become bright orange, and give up very little color to hydrochloric acid. In each case the original green color is restored by washing with water. From methyl green, Helvetia green is distinguished by the fibres not becoming violet when heated.

Light Green S F (bluish) and Light Green S F (yellow), are disulphonic acid derivatives of the benzaldehyde group. They are prepared by heating benzaldehyde with benzyldimethyl-(or diethyl) aniline and sulphonating the products so obtained by

means of fuming sulphuric acid; subsequent oxidation gives the dyestuffs. The yellow shade dyestuff is also met with under the names A c i d G r e e n SOF, A c i d G r e e n D, A c i d G r e e n JJ, and L i g h t G r e e n S, while the blue shade is sometimes called A c i d G r e e n and A c i d G r e e n M.

ADULTERATIONS OF ANILINE GREENS. Iodine-green varies much in price and quality, the commercial value not always following the dyeing properties, which in samples of the same price may vary as much as 50 per cent. Crystallized greens are usually purer than the amorphous kinds, but not always. Aniline greens vary much in tint, yellow shades being due to picric acid or other yellow dye, and green ones to soluble aniline blue. The latter, when present in small proportion, is best recognized by yellow light. Large amounts may be detected by treating the dye with picric acid and glycerin, when the green remains insoluble, and any blue admixture may be recognized by the color and characters of the filtered liquid. If the dye be the picrate of " verdaniline " mixed with soluble blue, mere treatment with water is sufficient to detect the admixture. Free picric acid may be detected by agitating with water and ether, and a picrate in the manner already described (page 118).

Some greens contain accidental admixtures of sodium acetate and black insoluble bodies, besides some aniline violet. Methyl green of good quality dissolves entirely in boiling alcohol. If a greenish-white residue be left, which turns violet when heated, it probably consists of the hydrochloride of n o n a m e t h y l - p a r a - l e u c a n i l i n e, $C_{19}H_{13}(CH_3)_6(CH_3Cl)_3$. This body is often present in considerable proportion in methyl-green which has not been purified by alcohol, and is sometimes added as an adulterant.

In water, methyl green should dissolve entirely with bluish-green color. A residue of green may consist of the picrate, which is entirely soluble in alcohol or dilute caustic soda. The aqueous solution of methyl green should yield no precipitate in the cold with dilute soda or sodium carbonate. A precipitate will probably consist of the base of methyl-violet, which after separation may be recognized by its color and reactions of its solution in hydrochloric acid. Its presence is due to defective purification of the coloring matter.

Intentional additions of sugar are occasionally made to aniline greens, and compounds of magnesium, lead, and chromium have been met with. Arsenic is found in some samples. Zinc chloride is a normal constituent of soluble and malachite greens.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Parafuchsin.	$C{\Large\langle}\begin{array}{l}(1)C_6H_4(4)NH_2\\(1)C_6H_4(4)NH_2Cl+4H_2O\\(1)C_6H_4(4)NH_2\end{array}$	Pure hydrochloride of pararosaniline.
Magenta Fuchsin Aniline Red.	$C{\Large\langle}\begin{array}{l}(1)C_6H_4(4\cdot NH_2\\(1)C_6H_4(4)NH_2Cl+4H_2O\\(1)C_6H_4(4)NH_2\end{array}$ & $C{\Large\langle}\begin{array}{l}(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH_2\end{array}\right.\\(1)C_6H_4(4)NH_2Cl+4H_2O\\(1)C_6H_4(4)NH_2\end{array}$	Mixture of hydrochloride and acetate of pararosaniline and rosaniline.
Acid Magenta. Fuchsin S. Rubin S.	$C{=}{\Large\langle}\begin{array}{l}(1)C_6H_3\left\{\begin{array}{l}(3)SO_3Na\\(4)NH_2\end{array}\right.\\(1)C_6H_3\left\{\begin{array}{l}(3)SO_3\\(4)NH_2\end{array}\right.{>}\\(1)C_6H_3\left\{\begin{array}{l}(3)SO_3Na\\(4)NH_2\end{array}\right.\end{array}$	Sulphonation of fuchsin.
Iso Rubin. New Fuchsin.	$C{=}{\Large\langle}\begin{array}{l}(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH_2\end{array}\right.\\(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH_2Cl\end{array}\right.\\(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH_2\end{array}\right.\end{array}$	. . .
Patent Blue V, U, extra, superfine.	$C{-}{-}(1)C_6H_2{\Large\langle}\begin{array}{l}(1)C_6H_4(4)N(C_2H_5)_2\\\left\{\begin{array}{l}(3)OH\\(4)SO_3-\frac{1}{2}Ca\\(5)SO_2O\end{array}\right.\\(1)C_6H_4(4)N(C_2H_5)_2\end{array}$	. . .
Diphenylamine Blue, spirit soluble.	$C{=}{\Large\langle}\begin{array}{l}(1)C_6H_4(4)NH.C_6H_5\\(1)C_6H_4(4)N.C_6H_5\\(1)C_6H_4(4)NH.C_6H_5.HCl\end{array}$	Phenylating pararosaniline.
Azuline.	Impure diphenylamine blue.	. . .
Methyl Blue.	$C(OH){\Large\langle}\begin{array}{l}(1)C_6H_4(4)NH.C_6H_4.SO_3Na\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\end{array}$	From diphenylamine blue.
Spirit Blue. Aniline Blue.	$C{=}{\Large\langle}\begin{array}{l}(1)C_6H_4(4)NH.C_6H_5\\(1)C_6H_4(4)N.C_6H_5\\(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH.C_6H_5.HCl\end{array}\right.\end{array}$	. . .
Soluble Blue.	$C(OH){\Large\langle}\begin{array}{l}(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH.C_6H_4.SO_3Na\end{array}\right.\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\end{array}$	From aniline blue.
Alkali Blue. Nicholson Blue.	$C(OH){\Large\langle}\begin{array}{l}(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)NH.C_6H_5\end{array}\right.\\(1)C_6H_4(4)NH.C_6H_5\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\end{array}$	From aniline blue.
Alkali Blue D.	$C(OH){\Large\langle}\begin{array}{l}(1)C_6H_4(4)NH.C_6H_5\\(1)C_6H_4(4)NH.C_6H_5\\(1)C_6H_4(4)NH.C_6H_4.SO_3Na\end{array}$	From diphenylamine blue.

CHARACTER OF DYESTUFF.	REACTIONS OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Green crystals; red solution.	Red ppt.	Yellow.	Yellow.	Colorless.	Soluble in alcohol. Basic dye.
Green crystals; red solution.	Decolorized. Red ppt.	Yellow.	Brownish-yellow.	Colorless.	Soluble in alcohol. Basic dye.
Green crystals; crimson solution.	Decolorized.	No change.	Yellow.	Red.	Slightly soluble in alcohol. Acid dye.
Green powder; red solution in hot water.	Red ppt.	Yellow.	Yellow.	Red.	Soluble in alcohol. Basic dye.
Copper-red powder; blue solution.	No change; violet on boiling.	Green, yellow.	Yellow.	Green.	Soluble in alcohol. Acid dye.
Brown powder; insoluble.		. .	Yellow.	Blue ppt.	Soluble in alcohol. Basic dye.
Dark blue coppery powder; insoluble in water.	Orange.	No change.	Yellow.	Blue ppt.	Soluble in alcohol. Obsolete. Basic dye.
Dark blue powder; blue solution.	Brown.	No change.	Brown.	Blue.	Basic dye.
Bronzy powder; insoluble.	Brown.	No change.	Yellow.	Blue ppt.	Soluble in alcohol. Basic dye.
Blue copper powder; blue solution.	Brown.	Slight ppt.	Orange.	Blue ppt.	Acid dye.
Dark blue powder; blue solution.	Brown.	Blue ppt.	Red.	Blue.	Soluble in alcohol. Acid dye.
Dark blue powder; blue solution in hot water.	Brown.	Blue ppt.	Brown.	Blue ppt.	Acid dye.

COMMERCIAL NAME.	FORMULA.	REMARKS
Bavarian Blue DSF.	$C(OH) \diagdown \begin{cases} (1)C_6H_4(4)NH.C_6H_4.SO_3Na \\ (1)C_6H_4(4)NH.C_6H_5 \\ (1)C_6H_4(4)NH.C_6H_4.SO_3Na \end{cases}$	From diphenylamine blue.
Victoria Blue B, BS.	$C \diagdown \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2.Cl \\ (1)C_{10}H_6(4)NH.C_6H_5 \end{cases}$	From phenyl-α-naphthylamine.
Victoria Blue 4 R.	$C \diagdown \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2.Cl \\ (1)C_6H_4(4)N \begin{cases} CH_3 \\ C_{10}H_7 \end{cases} \end{cases}$	. . .
Night Blue.	$C \diagdown \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N(C_2H_5)_2.Cl \\ (1)C_{10}H_6(4)NH.C_6H_4.CH_3 \end{cases}$	. . .
Alpine Blue. Fast Wool Blue.	$C \diagdown \begin{cases} (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)N(CH_3)_2 \end{cases} \\ (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)N(CH_3)_2 \end{cases} \\ (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3 \end{cases} \end{cases}$	. . .
Alkali Blue XG.	The sodium salts of the sulphonic acids of β-naphthylated rosaniline.	. . .
Soluble Blue XG.	Similar to preceding.	. . .
Methyldiphenyl-amine Blue.	$C \diagdown \begin{cases} (1)C_6H_4(4)N(CH_3)C_6H_5 \\ (1)C_6H_4(4)N(C_6H_5)HCl \\ (1)C_6H_4(4)N(CH_3)C_6H_5 \end{cases}$	From chloranil.
Höchst New Blue.	$C(OH) \diagdown \begin{cases} (1)C_6H_4(4)N(CH_3)C_6H_4SO_3Na \\ (1)C_6H_4(4)N(CH_3)C_6H_4SO_3Na \\ (1)C_6H_4(4)N(CH_3)C_6H_4SO_3Na \end{cases}$	. . .
Bradford Blue.	Hydrochloride of meta-amido-phenyl-ated rosaniline.	. . .
Glacier Blue.	$C \diagdown \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.CH_3 \end{cases} \\ (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NHCl.CH_3 \end{cases} \\ (1)C_6H_3Cl_2 \end{cases}$	. . .
Cyanol extra. Acid Blue 6 G.	$C(OH) \diagdown \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.C_2H_5 \end{cases} \\ (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.C_2H_5 \end{cases} \\ (1)C_6H_2 \begin{cases} (2)SO_3Na \\ (4)SO_3Na \\ (5)OH \end{cases} \end{cases}$	. . .
Cyanin B.	Not determined.	Oxidation of Patent Blue V.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Indigo-blue powder; blue solution.	Red.	Darker.	Brown.	Blue.	Blue dye for silk.
Bronzy powder; blue solution.	Brown ppt.	Blue ppt. soluble in excess.	Orange.	Blue.	Soluble in alcohol. Acid dye.
Bronzy powder; violet solution.	Brown ppt.	Blue ppt. soluble in excess.	Brown.	Blue.	Acid dye.
Bronzy powder; bluish - violet solution.	Brown ppt.	Blue ppt. soluble in excess.	Brown.	Blue.	Soluble in alcohol. Acid dye.
Violet powder; blue solution.	Blue ppt.	Yellow.	Green.	Blue.	Soluble in alcohol.
Black lumps; greenish - blue solution.	Black ppt.	Blue ppt.	Brown.	Blue ppt.	Acid dye.
Reddish powder; blue solution.	Claret.	Blue ppt.	Brown.	Blue ppt.	Acid dye.
Coppery lumps; insoluble.	Red (alcoholic solution).	No change (alcoholic solution).	Yellow.	Blue ppt.	Soluble in alcohol. Obsolete.
Dark blue powder; blue solution.	Decolorized.	Precipitate.	Red.	Blue ppt.	Slightly soluble in alcohol. Acid dye.
Bronzy powder; violet solution.	Brown ppt.	Blue ppt.	Brown.	Blue ppt.	Soluble in alcohol. Obsolete.
Violet powder; greenish - blue solution.	Orange.	Green ppt.	Yellow.	Green ppt.	Soluble in alcohol. Basic dye.
Dark blue powder; blue solution.	Red on boiling.	Yellow.	Yellow.	Blue.	Acid dye for wool.
Copper-red powder; blue solution.	Violet.	Yellow.	Yellow.	Green.	Acid dye for wool.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Patent Blue A.	$C \begin{cases} (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_5 \end{cases} \\ (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_5 \end{cases} \\ (1)C_6H_2 \begin{cases} (5)OH \\ (4)SO_3.\frac{1}{2}Ca \\ (2)SO_2.O \end{cases} \end{cases}$	. . .
Victoria Blue R. New Victoria Blue.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N.Cl.(CH_3)_2 \\ (1)C_{10}H_6(4)NH.C_2H_5 \end{cases}$	. . .
Chrome Blue.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_{10}H_5 \begin{cases} (\alpha)OH \\ CO_2H \end{cases} \end{cases}$	. . .
Methyl Violet B.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_4(4)NH.CH_3 \end{cases}$	Oxidation of dimethylaniline.
Crystal Violet.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_4(4)N(CH_3)_2 \end{cases}$	. . .
Benzyl Violet.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_4(4)N \begin{cases} CH_3 \\ CH_2.C_6H_5 \end{cases} \end{cases}$	From methyl violet.
Ethyl Violet.	$C \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N(C_2H_5)_2Cl \\ (1)C_6H_4(4)N(C_2H_5)_2 \end{cases}$	From diethylaniline.
Hoffmann Violet.	$C \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.C_2H_5 \end{cases} \\ (1)C_6H_4(4)NH.C_2H_5.Cl \\ (1)C_6H_4(4)NH.C_2H_5 \end{cases}$	. . .
Regina Purple.	$C \begin{cases} (1)C_6H_4(4)NH.C_6H_4.CH_3 \\ (1)C_6H_4(4)NH \\ (1)C_6H_4.NH_2 \end{cases}$	By-product from magenta.
Spirit Violet.	Hydrochloride of diphenyl-rosaniline (?).	. . .
Soluble Regina Violet.	Sodium salt of diphenyl-rosaniline-tri-sulphonic acid.	Action of sulphuric acid on preceding.
Red Violet 5 RS.	$C = \begin{cases} (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)NH.C_2H_5 \end{cases} \\ (1)C_6H_2 \begin{cases} (3)CH_3 \\ (4)NH_2 > \\ (5)SO_3 \end{cases} \\ (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)NH_2 \end{cases} \end{cases}$	From ethylrosaniline.
Red Violet 4 RS.	$C = \begin{cases} (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)NH.CH_3 \end{cases} \\ (1)C_6H_2 \begin{cases} (3)CH_3 \\ (4)NH_2 > \\ (5)SO_3 \end{cases} \\ (1)C_6H_3 \begin{cases} (3)SO_3Na \\ (4)NH.CH_3 \end{cases} \end{cases}$	From dimethylrosani-line.

| CHARACTER OF DYESTUFF. | REACTION OF AQUEOUS SOLUTION. | | REACTION OF DYE WITH SULPHURIC ACID. | | OTHER CHARACTERISTICS. |
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Copper-red powder; blue solution.	Violet on heating.	Green with precipitation of color acid.	Yellow.	Green with ppt. of color acid.	Soluble in alcohol. Acid dye for wool.
Blue powder; blue solution in hot water.	Brown ppt.	Brown ppt.	Yellow.	Green.	Basic dye. Soluble in alcohol.
Black paste; blue solution.	No change.	Brown.	Red.	Brown.	Soluble in alcohol. Mordant dye for wool.
Green metallic powder; violet solution.	Brown ppt. and color.	Brown.	Yellow.	Violet.	Soluble in alcohol. Basic dye.
Bronze crystals; violet solution.	Violet ppt.	Blue. green, finally yellow.	Yellow.	Green, blue, finally violet.	Soluble in alcohol. Basic dye.
Metallic powder; violet solution.	Brown ppt. and color.	Brown.	Yellow.	Violet.	Soluble in alcohol. Basic dye.
Green crystalline powder; violet solution.	Violet ppt. melting on heating.	Orange.	Yellow.	Green.	Basic dye.
Green crystalline powder; violet solution.	Brown ppt.	Yellow.	Brown.	Violet.	Basic dye.
Green powder; violet solution.	Brown ppt.	Brown, blue on dilution.	Brown.	No change.	Basic dye.
Green grains; violet solution.	Decolorized.	Green ppt.	Brown.	Violet ppt.	Soluble in alcohol. Basic dye.
Bronze powder; violet solution.	Lighter.	Violet ppt.	. .	. .	Acid dye for wool.
Violet metallic lumps; violet solution.	Yellow.	No change.	Yellow.	Violet.	Acid dye.
Violet powder; violet solution.	Orange.	No change.	Yellow.	Violet.	Acid dye.

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COMMERCIAL NAME.	FORMULA.	REMARKS.
Acid Violet 4 BN, 6 B.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N \begin{cases} CH_3 \\ CH_2.C_6H_4.SO_3Na \end{cases} \end{cases}$	Sensitive to alkalies.
Acid Violet 6 B (Berlin).	$C= \begin{cases} (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{cases} \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3 \end{cases} >O \end{cases}$	. . .
Formyl Violet S 4 B.	$C= \begin{cases} (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{cases} \\ (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_2 \end{cases} >O \end{cases}$	Used as a substitute for indigo-carmine.
Alkali Violet.	$C(OH) \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N \begin{cases} CH_3 \\ C_6H_4.SO_3Na \end{cases} \end{cases}$	May be dyed in alkaline, neutral or acid bath.
Chrome Violet.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_3 \begin{cases} (4)OH \\ (3)CO_2H \end{cases} \end{cases}$	. . .
Fast Acid Violet 10 B.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_3 \begin{cases} (2)SO_3Na \\ (4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3 \end{cases} \end{cases} \end{cases}$	. . .
Acid Violet 6 BW.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_2 \begin{cases} (2)O.C_2H_5 \\ (4)NH.C_6H_4.CH_3 \\ (5)SO_3Na \end{cases} \end{cases}$	. . .
Acid Violet 7 B.	$C(OH) \begin{cases} (1)C_6H_4(4)N \begin{cases} CH_3 \\ C_6H_4.SO_3Na \end{cases} \\ (1)C_6H_4(4)N \begin{cases} CH_3 \\ C_6H_4.SO_3Na \end{cases} \\ (1)C_6H_4(4)N(C_2H_5)_2 \end{cases}$	. . .
Methyl Green.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_3Cl+ZnCl_2 \\ (1)C_6H_4(4)N(CH_3)_3Cl \end{cases}$	From methyl violet.
Iodine Green.	$C \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)N(CH_3)_2 \end{cases} \\ (1)C_6H_4(4)N(CH_3)_2Cl+ZnCl_2 \\ (1)C_6H_4(4)N(CH_3)_2 \end{cases}$	From Hoffmann violet.
Malachite Green.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_5 \end{cases}$	From benzaldehyde.
Ethyl Green.	$C \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4)N(C_2H_5)_2.SO_4H \\ (1)C_6H_5 \end{cases}$	From benzaldehyde.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Violet powder; violet solution.	Blue ppt.	Blue ppt.	Yellow.	Blue.	Acid dye.
Violet powder; violet solution.	Light blue.	Bluish-green.	Brown.	Bluish-green.	Soluble in alcohol. Acid dye.
Violet powder; violet solution.	No change.	Violet ppt. soluble in excess.	Orange.	Blue.	Soluble in alcohol. Acid dye.
Violet powder; violet solution.	Blue ppt.	Violet ppt. soluble in excess.	Orange.	Green ppt.	Acid dye.
Black paste; insoluble.	Violet solution and black ppt.	Brown.	Brown.	Redder.	Soluble in alcohol. Mordant dye.
Grey powder; violet solution.	Yellow.	No change.	Orange.	Yellow.	Soluble in alcohol. Acid dye.
Violet powder; violet solution.	Decolorized.	Redder.	Orange.	Violet.	Soluble in alcohol. Acid dye.
Violet powder; violet solution.	Violet ppt.	Green.	Orange.	Violet.	Soluble in alcohol. Acid dye.
Green crystals; bluish - green solution.	Decolorized.	Orange.	Orange.	Green.	Basic dye. Obsolete.
Green fragments; bluish-green solution.	Decolorized.	Orange.	Orange.	Green.	Basic dye. Obsolete.
Green or yellow crystals; bluish-green solution.	Decolorized, and green ppt.	Orange.	Yellow.	Green.	Basic dye. Precipitated by picric acid. Soluble in alcohol.
Golden crystals; green solution.	Decolorized, and green ppt.	Orange.	Yellow.	Green.	Basic dye. Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Victoria Green 3 B.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_3Cl_2 \end{cases}$	From dichlorbenzaldehyde.
Helvetia Green.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)SO_3Na \\ (1)C_6H_4(4)N(CH_3)_2 \end{cases}$	From malachite green.
Guinea Green B.	$C(OH) \begin{cases} (1)C_6H_4(4)N \begin{Bmatrix} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \\ (1)C_6H_5 \\ (1)C_6H_4(4)N \begin{Bmatrix} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \end{cases}$	From benzaldehyde.
Light Green SF (bluish).	$C(OH) \begin{cases} (1)C_6H_4(4)N \begin{Bmatrix} CH_3 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \\ (1)C_6H_4(4)SO_3Na \\ (1)C_6H_4(4)N \begin{Bmatrix} CH_3 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \end{cases}$	From benzaldehyde.
Light Green SF (yellowish).	$C(OH) \begin{cases} (1)C_6H_4(4)N \begin{Bmatrix} CH_3 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \\ (1)C_6H_4(4)SO_3Na \\ (1)C_6H_4(4)N \begin{Bmatrix} CH_3 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \end{cases}$	From benzaldehyde.
Fast Green.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(3)N(CH_2.C_6H_4.SO_3Na)_2 \end{cases}$	From nitrobenzaldehyde.
Guinea Green BV.	$C(OH) \begin{cases} (1)C_6H_4(4)N \begin{Bmatrix} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \\ (1)C_6H_4(3)NO_2 \\ (1)C_6H_4(4)N \begin{Bmatrix} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{Bmatrix} \end{cases}$	From nitrobenzaldehyde.
Alkali Green. Viridine.	$C \begin{cases} (1)C_6H_5 \\ (1)C_6H_4(4)NH.C_6H_4.SO_3Na \\ (1)C_6H_4(4)NH.C_6H_5 \end{cases}$	From benzyl chloride and diphenylamine.
Azo-Green.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(3)N=N(1)C_6H_4 \begin{Bmatrix} (3)CO_2H \\ (4)OH \end{Bmatrix} \end{cases}$	From salicylic acid.
Chrome Green.	$C(OH) \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(3)CO_2H \end{cases}$	From benzoic acid.
Wool Green S.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2SO_3Na \\ (1)C_{10}H_6(2)OH \end{cases}$	. . .

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Green crystals; greenish-blue solution in hot water which gelatinizes on cooling.	Orange.	Yellow.	Yellow.	Green.	Soluble in alcohol. Basic dye.
Green powder; bluish-green solution.	Decolorized.	Brown ppt.	Yellow.	Green.	Obsolete. Soluble in alcohol. Acid dye.
Green powder; green solution.	Green ppt.	Yellow.	Yellow.	Green.	Soluble in alcohol. Acid dye. Green ppt. with $BaCl_2$.
Brown-black powder; green solution.	Decolorized; violet ppt.	Yellow.	Yellow.	Green.	Soluble in alcohol. Acid dye.
Green powder; green solution.	Decolorized; violet ppt.	Yellow.	Yellow.	Green.	Soluble in alcohol. Acid dye.
Bluish-green crystals; violet solution.	No change; with excess violet ppt.	Yellow.	Yellow.	Green, blue, and finally violet.	Soluble in alcohol. Acid dye.
Green powder; green solution.	Decolorized.	Green ppt.	Brown.	Green.	Soluble in alcohol. Acid dye.
Green powder; green solution.	Brown.	Green ppt.	Red.	Green ppt.	Obsolete. Soluble in alcohol.
Green paste; green solution.	Clear solution.	Red.	Brown.	Red ppt.	Soluble in alcohol. Mordant dye.
Brown powder; green solution.	Decolorized.	Orange.	Orange.	No change.	Soluble in alcohol. Mordant dye.
Violet powder; green solution.	Violet.	Yellow.	Violet.	Green.	Soluble in alcohol.

Rosolic Acid Derivatives.

If the amido-group in rosaniline be replaced by the hydroxyl-group, we obtain a body called r o s o l i c a c i d, which forms the base of a number of dyestuffs.

The carbinol $(HO)C{\Large<}\begin{smallmatrix}C_6H_4OH\\C_6H_4OH\\C_6H_4OH\end{smallmatrix}$ is unknown, but its anhydride

is met with in a u r i n, or pararosolic acid, which has the formula:

$$C{\Large<}\begin{smallmatrix}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.O\end{smallmatrix}$$
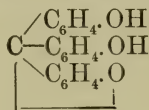
By heating phenol with oxalic and sulphuric acids a yellowish-red coloring matter is produced. The nature of the reaction was long misunderstood, but later researches have shown that at least two homologous bodies had been previously confounded, namely:—

Aurin, or Pararosolic Acid, $C_{19}H_{14}O_3$, or

$$\left\{\begin{smallmatrix}C_6H_4\\O—\end{smallmatrix}\right\}\ C\ \left\{\begin{smallmatrix}C_6H_4(OH)\\C_6H_4(OH)\end{smallmatrix}\right\};\ \text{and}$$

Rosaurin, Rosolic Acid, or Methyl-aurin, $C_{20}H_{16}O_3$, or

$$\left\{\begin{smallmatrix}C_6H_3(CH_3)\\O————\end{smallmatrix}\right\}\ C\ \left\{\begin{smallmatrix}C_6H_4(OH)\\C_6H_4(OH).\end{smallmatrix}\right\}$$
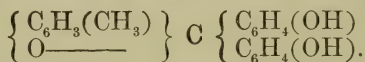
The formula expressing the formation of aurin is:—

$$3C_6H_6O + C_2H_2O_4 = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O.$$

Aurin and rosaurin may also be obtained by the action of nitrous acid on pararosaniline and rosaniline respectively:—

$$C_{20}H_{21}N_3O + 3HNO_2 = C_{20}H_{16}O_3 + 4H_2O + 3N_2.$$
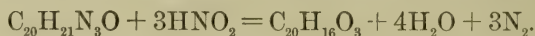
Or a dilute solution of aniline hydrochloride may be treated with sodium nitrite, when diazorosaniline chloride is formed, and then on adding sulphuric acid and boiling rosolic acid is produced.

Conversely, when aurin and rosaurin are heated with aqueous ammonia under pressure to 200° C. they are reconverted into pararosaniline and aniline respectively : — $C_{19}H_{14}O_3 + 3NH_3 = C_{19}H_{19}N_3O + 2H_2O.$

From these reactions it appears that aurin and rosaurin are derivatives of triphenylmethane, $CH(C_6H_5)_3.$

Pure aurin may be obtained from the commercial product by

passing ammonia gas through a saturated alcoholic solution of the latter, when steel-blue crystals of a m m o n i u m a u r a t e, $C_{19}H_{12}O.(ONH_4)_2$, are deposited, the impurities remaining in solution. The washed precipitate may be decomposed by dilute hydrochloric or acetic acid, or simply exposed to the air, when ammonia volatilizes and pure aurin remains.

When pure, aurin forms crystalline needles having an adamantine lustre and the color of chromic acid, or else of a darker shade with a blue or greenish-blue reflection. Aurin is fusible, but not volatile without decomposition.

Commercial aurin or rosolic acid contains an atom or two of water, and is a dark amorphous substance with a beetle-green lustre. The powder is red.

Aurin and rosaurin are but slightly soluble in water, though their solutions have a reddish-yellow color. They dissolve very readily in hot alcohol, somewhat sparingly in cold, and are also moderately soluble in glacial acetic acid, phenol, creosote, and in ether, but are insoluble in benzene and carbon disulphide.

Aurin and rosaurin dissolve readily in solutions of ammonia and fixed alkalies to form solutions which are bluish-red when dilute and yellowish-red when concentrated. A characteristic change in the absorption-spectrum occurs on dilution.

Aurin and rosaurin have the property of combining both with acids and bases. The former compounds are the more definite; but ether extracts aurin and rosaurin from its acidulated solutions and not from its alkaline solutions.

Solutions of aurin are decolorized when heated with sodium amalgam, or caustic soda and zinc-dust, colorless h y d r a u r i n, $C_{19}H_{16}O_3$, being formed. The alkaline solution is also decolorized by heating with excess of potassium cyanide, and on cooling and acidulating white crystalline flocks of h y d r o c y a n a u r i n, $C_{20}H_{15}NO_3$, are thrown down.

YELLOW CORALLIN. This coloring matter is prepared by treating 8 parts of pure phenol in the cold with 3.2 parts of strong sulphuric acid, and after some hours adding 4.8 parts of oxalic acid, and heating the whole to 110° for twenty-four hours. In addition to aurin and methyl-aurin, more or less o x i d i z e d a u r i n, $C_{19}H_{16}O_{31}$, and pseudo-rosolic acid or c o r a l l i n - p h t h a - l e ï n, $C_{20}H_{16}O_4$, are also produced, and a sublimate of p h e n y l o x a l a t e has been observed to be formed. The melt is poured into water and purified by treatment with boiling water. The

product is yellow corallin, and forms a brown resinous substance having a green metallic lustre. It contains about 20 per cent. of aurin, besides crystalline derivatives of rosolic acid, and resinous bodies. Its reactions are identical with those of aurin. The soluble sodium salt of red corallin is also called "yellow corallin."

RED CORALLINE or PEONIN is prepared by heating two parts of yellow corallin with one of strong ammonia to 120°–140° C., when one of the hydroxyl groups is replaced with formation of the substance, $C_{19}H_{13}O_2(NH_2)$, which is precipitated on pouring the liquid into water and acidifying. The product is "spirit soluble" red corallin; "water soluble" corallin being the ammonium salt. The first forms lumps with a metallic lustre; the latter a brownish-red porous mass, soluble in concentrated sulphuric acid with yellow color. The red aqueous solution of the ammonium salt is unaltered by alkalies and precipitated yellow by acids. Basic lead acetate and aluminium acetate produce orange or yellow precipitates.

Eupittonic acid has the constitution of a h e x a - m e t h y l - a u r i n, but as a dyestuff it is now obsolete.

DETECTION OF AURIN, &c.

Aurin and its allies are readily recognized by their physical characters, and by dissolving in strong sulphuric acid with yellow color, no vapors of bromine or iodine being evolved on heating, either with or without the addition of manganese dioxide. If not readily soluble in water alone, they dissolve in dilute ammonia with non-fluorescent purple-red color, which is not removed by agitation with ether. On acidulating, the red solution is changed to yellow, a yellow precipitate being formed in strong solutions. This is readily soluble in ether. with yellow color, and on separating the ethereal layer and agitating it with ammonia the latter acquires a deep red color. Solutions of aurin are immediately decolorized by hypochlorites, or by boiling with zinc-dust and ammonia, the red color being restored in the latter case on adding potassium ferricyanide.

Aurin and its allies are not now used in dyeing, as the yellow or orange-red shades produced are very perishable; its chief use is for coloring varnishes and lacquers. The coloring matter on printed fabrics is turned yellow by acids, and readily removed by ammonia, the solution being purple-red. On acidulating this liquid with acetic acid, and heating in it a tuft of gun-cotton, the latter is dyed yellow.

COMMERCIAL NAME.	FORMULA.	REMARKS.	CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
				With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Aurin.	$C\Big\langle \begin{matrix}(1)C_6H_4(4)OH\\(1)C_6H_4(4)O\\(1)C_6H_4(4)OH\end{matrix}$ (p—Rosolic Acid.)	From phenol by action of oxalic and sulphuric acids.	Brown lumps; insoluble in water.	Cherry - red (alcoholic solution).	No change.	Yellow.		Soluble in alcohol.
Yellow Corallin.	Sodium salt of Aurin.		Metallic lumps; red solution.	No change.	Yellow solution with ppt.	Yellow.	Yellow ppt.	Soluble in alcohol.
Peonin, Corallin, Aurin R.	$C\Big\langle \begin{matrix}(1)C_6H_4(4)OH\\(1)C_6H_4(4)NH\\(1)C_6H_4(4)OH\end{matrix}$	Action of ammonia on aurin.	Brown powder; red solution in hot water.	No change.	Yellow.	Yellow.		Soluble in alcohol.
Aurotin.	$C=\begin{matrix}(1)C_6H_2\begin{Bmatrix}(4)ONa\\(3)NO_2\\(5)NO_2\end{Bmatrix}\\(1)C_6H_2\begin{Bmatrix}(4)O\\(3)NO_2\\(5)NO_2\end{Bmatrix}\\(1)C_6H_4(2)CO_2Na\end{matrix}$	From phenol-phthalein.	Yellow powder; yellow solution.	No change.	Precipitate.			Soluble in alcohol. Acid or mordant dye for wool.
Chrome Violet.	$C=\begin{matrix}(1)C_6H_3\begin{Bmatrix}(4)OH\\(3)CO_2Na\end{Bmatrix}\\(1)C_6H_3\begin{Bmatrix}(4)O\\(3)CO_2Na\end{Bmatrix}\\(1)C_6H_3\begin{Bmatrix}(4)OH\\(3)CO_2Na\end{Bmatrix}\end{matrix}$	From salicylic acid.	Brown powder; red solution.	Brown.	Precipitate.	Brown.	Precipitate.	Used in calico-printing.

Phthaleïns.

The phthaleïns are bodies produced by the reaction of phthalic acid or anhydride on phenols, with elimination of water. At a moderate temperature, two molecules of the phenol react with one of phthalic acid or anhydride, a "phthaleïn" being formed, thus:—

$$C_6H_4 \left\{ \begin{matrix} CO.OH \\ CO.OH \end{matrix} \right. + 2C_6H_4(H).OH = C_6H_4 \left\{ \begin{matrix} CO.C_6H_4.OH \\ CO.C_6H_4.OH \end{matrix} \right. + 2OH_2.$$
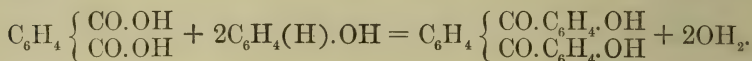
The product, p h e n o l - p h t h a l e ï n, is a derivative of triphenylmethane, and hence is allied to pararosaniline and aurin, as is evidenced by the following structural formula:
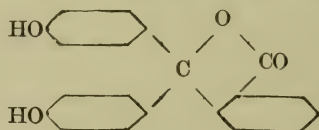
and the sodium salt of phenolphthaleïn is represented by:
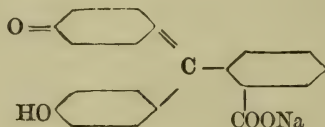
At a higher temperature, by the reaction of one molecule of each body, o x y a n t h r a q u i n o n e, a derivative of anthracene, is formed:—

$$C_6H_4 \left\{ \begin{matrix} CO.OH \\ CO.OH \end{matrix} \right. + C_6H_5.OH = C_6H_4 \left\{ \begin{matrix} CO \\ CO \end{matrix} \right\} C_6H_3.OH + 2OH_2.$$
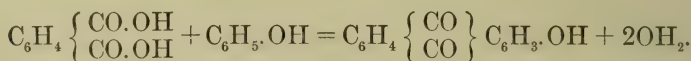
As a class, the phthaleïns are weak acid bodies, nearly insoluble in water, but soluble in alcohol and readily so in ether. Their salts with the alkali-metals are soluble and strongly colored. By the action of nascent hydrogen, the phthaleïns assimilate H_2 and are converted into the corresponding p h t h a l i n s, which are colorless bodies absorbing oxygen from the air with re-formation of phthaleïns. The phthaleïns of phenol, resorcinol, and pyrogallol are the most important.

Phenol-phthaleïn. Dihydroxy-diphenyl-phthalide.

$$C_{20}H_{14}O_4 = C_6H_4 \left\{ \begin{matrix} CO.C_6H_4(OH).^p \\ CO.C_6H_4(OH).^p \end{matrix} \right.$$
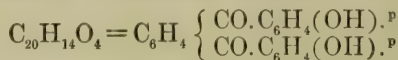
As already stated, phenol-phthaleïn results from the reaction of phenol on phthalic acid or anhydride.[1]

Phenol-phthaleïn is not used in dyeing, and derives its chief interest from the magnificent pink coloration which its solution acquires by the action of alkalies, the smallest trace of which may thus be detected. On the other hand, the weakest acids destroy the color, so that such bodies as potassium stearate, potassium cyanide, and sodium bicarbonate ($NaHCO_3$) are neutral in their reaction to it.

The same is true of cold aqueous solutions of the bodies represented by the following formulæ: — $KHCO_3$, $Na_2S_2O_3$, Na_2SO_3, $NaHS$, Na_2HPO_4, Na_2HAsO_4, $NaNO_2$, K_2CrO_4, $K_2C_2O_4$, $KNaC_4H_4O_6$, $Na_3C_6H_5O_7$. In all these cases the point of neutrality is indicated extremely sharply, and the same remark applies to the titration of acetic, butyric, and valeric acids. No small advantage possessed by phenol-phthaleïn is that it reacts perfectly in alcoholic and even ethereo-alcoholic solution, and hence allows of the accurate titration of many insoluble organic acids, including palmitic, stearic, oleic, linoleic, ricinoleic, the acids of colophony (pinic, pimaric, sylvic), etc. The alkaloids have generally no marked alkaline reaction on phenol-phthaleïn, and hence the amount of acid in salts of morphine, quinine, cinchonine, quinidine, brucine, aniline, and urea, operating, if necessary, in alcoholic solution, can be ascertained by titration with standard acid, just as if no organic base were present.

The value of phenol-phthaleïn as an indicator of neutrality is completely vitiated by the presence of ammonium salts.

Phenol-phthaleïn is readily soluble in alcohol. A one per cent. solution keeps perfectly, and a few drops are sufficient for each titration.

Further information respecting the use of phenol-phthaleïn as an indicator of neutrality will be found in the section on ''Litmus.''

Fluoresceïn. $C_{20}H_{12}O_5 = C_6H_4 \left\{ \begin{matrix} CO.C_6H_3(OH) \\ CO.C_6H_3(OH) \end{matrix} \right\} O.$

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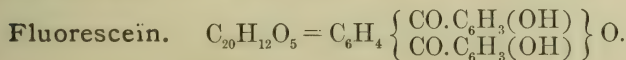
[1] Five parts of phthalic anhydride, ten of phenol, and four of concentrated sulphuric acid should be heated together to 120° C. for 10 hours. The product is boiled with water, and the residue dissolved in dilute soda. On filtering the liquid, the anhydride remains behind, while the phenol-phthaleïn itself is precipitated on treating the filtrate with acetic acid and a little hydrochloric acid. It may be purified by dissolving in alcohol, boiling with animal charcoal, and reprecipitating by diluting the liquid with boiling water.

This body is the a n h y d r i d e o f r e s o r c i n o l - p h t h a l e ï n, $C_{20}H_{14}O_6$ (see last page). Structurally, it may he represented by the formula:
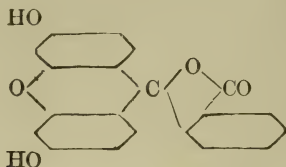
It is prepared by heating three parts of phthalic anhydride and four of resorcinol to 200°–210° for one hour, or till no more steam is evolved and the melt has become solid.[1] The product is purified by solution in soda and addition of phosphate of sodium and chloride of calcium to the solution, when the phosphate of calcium carries down the impurities, and the fluorescëin may be precipitated by acidulating the filtrate.

Fluorescëin forms an amorphous yellow precipitate which becomes crystalline and yellowish-red on standing or drying, and then contains $C_{20}H_{12}O_5 + H_2O$. It is nearly insoluble in cold water, more readily in acidulated, and sparingly in hot water, to which it imparts a yellow color. When freshly precipitated it dissolves readily in alcohol and ether, but is nearly insoluble in benzene and chloroform. The ethereal solution is pale yellow and non-fluorescent, while the yellowish-red alcoholic solution shows a green fluorescence.

Fluorescëin is a feeble acid, dissolving in alkalies with dark red color. The strong alkaline solution is not fluorescent, but on dilution it changes to reddish-yellow and yellow, and then exhibits a magnificent yellowish-green fluorescence, similar to that of uranium glass, and gives an absorption-spectrum with a broad dark band in the green. Even if the solution be so dilute as to appear colorless by transmitted light, the green bloom is still visible.[2]

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[1] For a valuable description of the manufacture of fluorescëin and eosin dyes, see a paper by O. M ü h l h a u s e r, *Jour. Soc. Dyers, etc.*, iii. 28, 63, translated from *Dingler's Polyt. Journal.*

[2] The beautifully fluorescent fountain shown by I. Levinstein, in the Chemical Section of the Manchester Jubilee Exhibition, was fed by water containing 1 part per million of fluorescëin. The intensity of the fluorescence may be employed for tracing the course of underground rivers and detecting the pollution of the water of wells by sewage, etc. By this means an underground connection was proved to exist between the Danube and the Ach, a small river flowing into Lake Constance.

When a solution of fluoresceïn in caustic soda is heated with zinc-dust the liquid becomes colorless and contains f l u o r e s c i n, $C_{20}H_{14}O_5$. On filtering from the excess of zinc and exposing the liquid to the air, it gradually re-acquires its reddish color, owing to the absorption of atmospheric oxygen and re-formation of fluoresceïn. Or if the colorless liquid be acidulated and agitated with ether, the fluorescin is dissolved, and on evaporating the ether is left as a colorless varnish, soluble without coloration in soda to form a liquid which rapidly turns red in the air from formation of fluoresceïn. The oxidation is immediate on addition of a ferri-cyanide to the alkaline liquid.[1]

Fluoresceïn dyes silk and wool yellow, but the colors are not fast. It forms insoluble lakes with silver, lead, etc., which compounds are not poisonous, and hence may be used for coloring toys, india-rubber goods, etc.

BENZYL-FLUORESCEÏN, $C_{20}H_{10}O_3(OC_7H_7)OH$, is produced by heating benzyl-resorcinol with phthalic acid and strong sulphuric acid. Its s o d i u m   s a l t constitutes the dye-stuff known as

CHRYSOLIN or URANIN.[2] A reddish-brown powder possessing a greenish reflex. Its aqueous and alcoholic solutions are yellowish-brown, and exhibit a remarkable green fluorescence, which disappears with formation of a brown-yellow precipitate of b e n z y l-f l u o r e s c e ï n on addition of acids. The precipitate is soluble in ether. The aqueous solution is darkened by alkalies, and the solid dye dissolves in strong sulphuric acid with yellow color, and yields a yellow precipitate on dilution. With stannous chloride and with lead salts, chrysolin gives brilliantly colored lakes. It dyes silk or wool a fast yellow, and is employed in cotton-dyeing for topping quercitron-yellow, the quercitron itself acting as a mordant.

[1] F l u o r a n is a substance very similar to fluoresceïn in its chemical nature, as may be seen by its formula:
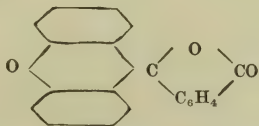
It occurs as a by-product in the crude melt in the manufacture of phenolphthaleïn.

[2] The name u r a n i n is also applied to the sodium salt of fluoresceïn or methylfluoresceïn. It forms a yellowish-brown powder, the aqueous solution of which fluoresces yellowish-green.

Substituted Fluoresceïns.   Eosins.[1]

A series of interesting and practically important coloring matters can be obtained by substituting the halogens, nitryl, or the alcohol-radicals for some of the hydrogen atoms of fluoresceïn.

TETRABROMFLUORESCEÏN, or ACID EOSIN, $C_{20}H_3Br_4O_5$, is prepared by gradually adding 24 parts of bromine to 10 parts of fluoresceïn dissolved in eight times its weight of strong alcohol.   When half the bromine has been added, changes from reddish-brown to a very dark brown color.   This marks the formation of the d i b r o m o- d e r i v a t i v e,[2] which is easily soluble in alcohol.   On continuing the addition of bromine the tetrabromfluoresceïn separates as a brick-red crystalline precipitate, which is washed with a little alcohol and then with water.   An alternative method of preparation is to mix a solution of fluoresceïn in caustic soda with a solution of the calculated amount of bromine in caustic soda, and then acidulate the liquid with hydrochloric acid, when the tetrabromfluoresceïn is precipitated.

Tetrabromfluoresceïn closely resembles fluoresceïn itself.   It is nearly insoluble in water, and its reddish-yellow solution in alcohol is not fluorescent (distinction from fluoresceïn).   It is a well-defined dibasic acid, the salts of which are decomposed by mineral acids, but only imperfectly by acetic acid.

By cautious treatment with caustic potash, acid eosin yields the p o t a s s i u m   s a l t, $C_{20}H_6Br_4O_5K_2 + 6aq$, which is known in commerce as *soluble eosin*, and forms a red powder or brownish-red crystals with blue or yellowish-green reflection.   It is not easily soluble in absolute alcohol, but dissolves completely in two or

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[1] The substituted fluoresceïns are now regarded as possessing a quinonoid structure instead of the older lactone formula ; $C = C_6H_4 = O$ with $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4.CO_2H} > O$ being   the   type   of   the

eosins, and $C = C_6H_4 = N \equiv$ with $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4.CO_2H} > O$ representing   the   rhodamines.   The   pyronines   or

formo-rhodamines have an analogous constitution :

$$HC \genfrac{}{}{0pt}{}{C_6H_3 - NR_2}{C_6H_3 = NR_2Cl} > O$$
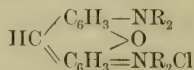
[2] The sodium salt of dibromfluoresceïn, always mixed with more or less of the tetrabrominated derivative, is known in commerce as *eosin-orange*.

three times its weight of water to form a reddish-yellow solution. This on dilution becomes rose-colored and exhibits an intense yellowish-green fluorescence, which is rendered still stronger by the addition of alcohol. The absorption-spectrum shows a broad dark band in the green, destroyed by mineral acids, but not by acetic acid. On adding hydrochloric acid the solution becomes yellow, and on heating gives a yellow precipitate of tetrabrom-fluorescein, which may be extracted by ether and removed from the ethereal solution by agitation with an alkali.

The s o d i u m   s a l t of the tetrabromfluorescein is an article of commerce under the name of *Eosin C*,[1] or in the form of garnet-red crystals as *Eosin B extra*. It closely resembles the potassium salt. The a m m o n i u m   s a l t, known as *Eosin B*, of a *red* appearance, is prepared by the direct action of ammonia gas on tetrabrom-fluorescein.[2]

By the addition of a soluble salt of eosin to solutions of the heavy metals, sparingly soluble or insoluble lakes are obtained as precipitates. Silver gives red, and zinc, cobalt, iron, manganese, bismuth, and tin reddish-yellow lakes.

A bright vermilion lake may be obtained by mixing the solution of eosin with starch or kaolin and precipitating with alum. If excess of alkali be previously added to the solution, the precipitate obtained is carmine-red, and with still more alkali a pink lake results. From yellowish shades sulphate of zinc or magnesium should be used in conjunction with alum.

Vermilionette is a brilliant lake obtained by precipitating eosin by lead acetate. Lighter shades are obtained by adding soda. A very bright vermilion-colored product is obtained by stirring up red-lead with an alkaline solution of eosin and then adding lead acetate to complete precipitation. Basic chromate of lead (chrome-red) gives even a brighter red than red-lead. Vermilionette sometimes contains a considerable proportion of barium sulphate or other diluent.

TETRAIODFLUORESCEIN, or IODEOSIN, $C_{20}H_8I_4O_5$, is prepared by mixing solutions of fluorescein and iodine in caustic soda, and then adding acetic acid. Its alkaline salts are sold as *eosin blue-shade* (soluble in water), *eosin J, erythrosin, erythrosin B, pyrosin B,*

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[1] Also known as: *Eosin yellowish, Eosin GGF, Water Soluble Eosin, Eosin A. Eosin 3J, and Eosin 4J, Eosin KS, Eosin DH, and Eosin JJF.*

[2] *Eosin Orange, Eosin 3G, Salmon Pink*, etc., are mixtures of di- and tetra-bromfluorescein.

iodeosin B, dianthin B, soluble primrose, and *erythrosin D.*[1] The sodium salt is brown-red and the ammonium salt light brick-red. Their aqueous solutions are not fluorescent (distinction from the brominated eosins), and on treatment with zinc-dust and ammonia the iodine is eliminated and a colorless solution of fluorescin obtained, turning red on exposure to air, with formation of fluorescëin.   *Erythrosin G* is the sodium or potassium salt of diodofluorescëin.

DIBROMO-DINITROFLUORESCEÏN, or NITROBROMEOSIN, $C_{20}H_8(NO_2)_2 Br_2O_5$, is produced by the action of dilute nitric acid on tetrabromfluorescëin dissolved in glacial acetic acid, or by acting with bromine on dinitrofluorescëin in alcoholic solution.   The salts are known in commerce as *safrosin, eosin scarlet, daphnin, eosin BN, methyl eosin, eosin scarlet B, eosin B, scarlet J, JJ,* and *V, nopalin, eosin scarlet BB, eosin BW, imperial red,* and *eosin DHV.*   The potassium and sodium salts are dark brown or green powders, while the ammonium salt is red. A mixture of bromonitrofluorescëin with the di- and tetra-nitro-derivatives is known as *lutécienne.   Rubeosin* is a nitrochlorofluorescëin, obtained by the action of nitric acid on *aureosin,* which is itself a chlorinated fluorescëin.

TETRABROMO-DICHLOROFLUORESCEÏN, $C_{20}H_6Cl_2Br_4O_5$.   In all the substituted fluorescëins hitherto described the replaced hydrogen belongs to the resorcinol residue, but eosins may also be prepared in which the hydrogen atoms of the phthalic acid residue are replaced.   Thus when dichlorphthalic acid reacts on resorcinol a dichlorofluorescëin is obtained, and by brominating or iodinating this body other coloring matters result.   *Rose Bengale*[2] and *phloxin*[3] are dyes of this kind, the former being the potassium or sodium salt of tetraiodo-dichlorofluorescëin, and the latter the potassium salt of tetrabromo-dichloro- (or tetrachloro-) fluorescëin.   *Cyanosin* is the potassium salt of the methyl or ethyl ether of phloxin.   *Phloxin TA (eosin 10B, erythrosin B)* is the sodium salt of tetrabromtetrachlorfluorescëin.

ETHERS OF SUBSTITUTED FLUORESCEÏNS.   The methyl and

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[1] Some of these names are applied to the alkaline salts of a di-iodfluorescëin, $C_{20}H_{10}I_2O_5$.

[2] Known also as *Rose Bengale N, AT, G.*

[3] Known also as *Phloxin P, Erythrosin BB,* and *New Pink.*

ethyl ethers of tetrabromfluorescein are obtained by heating eosin with methyl or ethyl alcohol and sulphuric acid, by heating acid eosin with methyl or ethyl bromide, or by brominating fluorescein in hot alcohol, when etherification and bromination occur simultaneously. The potassium salt of ethyl-tetrabromfluorescein is a red crystalline substance with a greenish reflex. It has found a considerable application in silk-dyeing, and is known as *spirit-eosin, ethyl-eosin, rose JB., spirit primrose, eosin BB, eosin S,* etc. *Methyl-eosin* is of very similar character.

Methyl- and ethyl-eosin are sparingly soluble in water and insoluble in absolute alcohol, but they dissolve easily in proof-spirit, the dilute solutions having a beautiful fluorescence.

Benzyl-fluorescein, or *chrysolin,* has already been described (page 317).

Cœrulein and *Cœrulein S,* are probably derivatives of alizarin, although it is made by heating gallein with concentrated sulphuric acid. Although insoluble in water, cœrulein gives a red solution on being heated with zinc-dust and ammonia. This solution contains a leuco-compound, which is readily reoxidized by exposure to the air to cœrulein.

REACTIONS OF THE EOSINS.

In referring to the various substituted fluoresceins, the systematic names are inconveniently long, while the commercial names are not always sufficiently distinctive. In such cases the terms brom-eosin, idoeosin, ethyl-eosin, etc., may be used with advantage.

The fluorescence of the eosins is most intense in alcoholic solutions (preferably containing a little free ammonia). It is strongest in the eosin-ethers (eosins soluble in alcohol), and then in bromeosin. Nitrobromeosin (safrosin) is but slightly fluorescent, but somewhat more so in presence of ammonia, while iodeosin does not fluoresce at all in aqueous and but little in alcoholic solution.

The absorption-spectra of aqueous and ammoniacal solutions of the eosins have been studied by C. H. Bothamley (*Jour. Soc. Chem. Ind.,* vi. 422), and exhibit some interesting peculiarities.

The eosins dissolve in cold concentrated sulphuric acid with yellow or orange color, which generally becomes darker on heating. Bromeosin and nitrobromeosin are turned dark red, and on adding water a new coloring matter separates out in dark flakes. On heating iodeosin with strong sulphuric acid, iodine is liberated, and bromine vapors are evolved from brominated eosins, especially if manganese dioxide be added.

On adding hydrochloric acid to solutions of the eosins, the corresponding free substituted fluoresceïns are precipitated. In all cases the precipitates are soluble in ether, and on agitating the separated ethereal solution with soda or ammonia the eosin passes into the alkaline liquid with characteristic color, and usually with fluorescence.

R. Benedikt (*Jour. Soc. Chem. Ind.*, ii. 170) has published a systematic scheme for the examination and identification of the various eosin dyes. Besides noting the solubility of the substance, the color and the fluorescence of the solution, and the shade produced on silk, he notes the behavior of the coloring matter when reduced. For this purpose, Benedikt directs that a few drops of a moderately concentrated solution of the dye should be diluted with water, and shaken in the cold with small quantities of zinc-dust and ammonia. All eosins are rapidly decolorized by this treatment. The decolorized and filtered solution usually re-oxidizes very gradually on exposure to the air, but more rapidly if it be well boiled till a copious precipitation of hydrated oxide of zinc occurs, and the liquid be then treated with sufficient hydrochloric acid to dissolve this precipitate, and an excess of ammonia again added. Another means of discrimination employed by Benedikt consists of treating a little of the coloring matter with a strong solution of caustic potash (1.3 sp. gr.).

By the reduction-test, *Eosin G* (bromeosin) gives a nearly colorless filtrate immediately after treatment with zinc and ammonia, being reduced to colorless tetrabromfluoresceïn. After boiling the liquid and treating with acid and ammonia as described above, the solution becomes cherry-red or crimson, with yellowish-green fluorescence; or, in other words, the original coloring matter is reformed. With potash solution, bromeosin gives in the cold an orange-red solution, which on boiling becomes purple-red, violet, and pure blue, with a *strong* green fluorescence. If the boiling has been continued long enough, the characters are unchanged by dilution.

Eosin J (iodeosin) loses its iodine when treated with zinc-dust and ammonia, and is converted into colorless fluorescin, which on oxidation, boiling, &c., is converted into fluoresceïn, the solution of which is reddish-yellow with a strong green fluorescence. The production of a highly fluorescent solution from a non-fluorescent one by reduction and subsequent oxidation is highly characteristic of iodeosin. On boiling with potash, eosin B first turns purple-

red and then blue-violet, with a feeble green fluorescence. On dilution, the liquid becomes purple-red.

Safrosin (nitrobromeosin), on treatment with zinc-dust and ammonia, is reduced to colorless fluorescin, and the NO_2 groups are simultaneously reduced. The filtered liquid oxidizes again with great rapidity, with formation of a cherry-red, non-fluorescent solution. With potash, safrosin becomes lighter and yellower, and on boiling turns olive-green, without fluorescence. When a little solid safrosin is heated on platinum foil, it swells up enormously after the manner of a " Pharaoh's serpent."

The *spirit-soluble eosins* behave with zinc and ammonia like bromeosin. They are insoluble in strong potash solution in the cold, but on boiling the reactions of bromeosin are gradually produced.

The eosins are often found in admixture with other coloring matters. Thus *nepaline* and *imperial scarlet* are mixtures of eosins with n a p h t h o l - y e l l o w, and *coccine* is a mixture of safrosin and a u r a n t i a. Such mixtures yield scarlets which are employed as cochineal substitutes. Naphthol-yellow and aurantia differ from the eosins in yielding colorless solutions by treatment with zinc and hydrochloric acid, which solutions do not again become colored on exposure to air, either with or without the addition of ammonia or sodium acetate. When heated, the nitro-compounds deflagrate without disengaging colored vapors. To induce deflagration it is sometimes necessary to mix the substance with a little oxide of lead.

Aurin and its allies present a somewhat close analytical resemblance to the eosins; but their ammoniacal solutions are not fluorescent, and no bromine or iodine vapors are evolved on heating the substance with sulphuric acid and manganese dioxide.

The eosins produce on silk and wool all shades of color from a reddish-orange to a cherry-red and purple. The yellowish shade is produced by eosin G, and the bluest by bengal red. For dyeing cotton with eosins, the fabric is mordanted with alumina or tin for yellow shades, and with lead salts for blue shades. The colors produced are not so fast as those on wool or silk, and are affected by light.

The eosins soluble in water are slightly removed when *fibres* dyed with them are treated with warm water, especially if a little ammonia be added. Spirit-soluble eosins are not affected by water, but are dissolved from the fibre by alcohol, which leaves the eosins soluble in water.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Phenolphthaleïn	$C\begin{cases}(1)C_6H_4(4)OH \\ (1)C_6H_4(4)OH \\ (1)C_6H_4(2)CO.O\end{cases}$	From phthalic anhydride.
Eosin.	Probably: $C = \begin{cases}(1)C_6H\begin{cases}(3)Br\\(4)ONa\\(5)Br\\(6)\\(6)>O\\(5)Br\\(4)O\\(3)Br\end{cases}\\(1)C_6H_4(2)CO_2Na\end{cases}$	From fluoresceïn.
Eosin J. Erythrosin.	$C = \begin{cases}(1)C_6HI_2\begin{cases}(4)ONa\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_4(2)CO_2Na\end{cases}$	From fluoresceïn.
Safrosin.	$C = \begin{cases}(1)C_6H(NO_2)(Br)\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_4(2)CO_2K\end{cases}$	From dibromfluoresceïn.
Phloxin.	$C = \begin{cases}(1)C_6H(Br_2)\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\C_6H_2(Cl_2)(2)CO_2K\end{cases}$	From dichlorfluoresceïn.
Rose Bengale.	$C = \begin{cases}(1)C_6HI_2\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_2Cl_2(2)CO_2K\end{cases}$	From dichlorfluoresceïn.
Methyl Eosin. Erythrin.	$C = \begin{cases}(1)C_6HBr_2\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_4(2)CO.OCH_3\end{cases}$	From eosin.
Ethyl Eosin. Rose J. B.	$C = \begin{cases}(1)C_6HBr_2\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_4(2)CO.OC_2H_5\end{cases}$	From eosin.
Cyanosin. Methyl Phloxin.	$C = \begin{cases}(1)C_6HBr_2\begin{cases}(4)OK\\(6)\\(6)>O\\(4)O\end{cases}\\(1)C_6H_2Cl_2(2)CO.OCH_3\end{cases}$	From phloxin.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Yellow crystals; insoluble.	Red solution.	Colorless.	Brown.	Precipitate.	Used as an indicator. Soluble in alcohol.
Bluish-red crystals; bluish-red solution, green fluorescence.	No change.	Orange ppt.	Yellow.	Orange ppt.	Soluble in alcohol, green fluorescence. Neutral dye.
Brown powder; red solution, no fluorescence.	No change.	Yellow ppt.	Yellow.	Yellow ppt.	Neutral dye.
Brown crystals; orange solution, faint fluorescence.	No change.	Green ppt.	Yellow.	Yellow ppt.	Neutral dye.
Yellow powder; red solution, green fluorescence.	Bluer.	Yellow ppt.	Yellow.	Brown ppt.	Neutral dye.
Brown powder; red solution, no fluorescence.	No change.	Red ppt.	Yellow.	Red ppt.	. . .
Green powder; red solution in hot water.	Darker.	Yellow ppt.	Yellow.	. .	Soluble in alcohol.
Brown powder; red solution, faint fluorescence.	Yellow ppt.	Brown ppt.	Yellow.	. .	. . .
Red powder; insoluble.	No change (alcoholic solution).	Fluorescence disappears (alcoholic solution).	Yellow.	Brown ppt.	Soluble in alcohol, yellow fluorescence.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Chrysolin.	$C=(1)C_6H_2\begin{cases}(3)CH_2.C_6H_5\\(4)ONa\\(6)\\(6)\end{cases}>O$ $(1)C_6H_3\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6H_4(2)CO_2Na$	From phthalic anhydride.
Uranin. Fluorescein.	$C=(1)C_6H_3\begin{cases}(4)ONa\\(6)\end{cases}>O$ $(1)C_6H_3\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6H_4(2)CO_2Na$	From phthalic anhydride.
Erythrosin G.	$C=(1)C_6H_2I\begin{cases}(4)OK\\(6)\end{cases}>O$ $(1)C_6H_2I\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6H_4(2)CO_2K$	From fluorescein.
Cyclamin.	$C=(1)C_6HBr_2\begin{cases}(4)OK\\(6)\end{cases}>S$ $(1)C_6HBr_2\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6H_2Cl_2(2)CO_2K$	From thionated dichlorfluorescein.
Phloxin TA. Erythrosin B.	$C=(1)C_6HBr_2\begin{cases}(4)ONa\\(6)\end{cases}>$ $(1)C_6HBr\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6Cl_4(2)CO_2Na$	From tetrachlorphthalic acid.
Rose Bengale 3 B, B.	$C=(1)C_6HI_2\begin{cases}(4)OK\\(6)\end{cases}>O$ $(1)C_6HI_2\begin{cases}(6)\\(4)O\end{cases}$ $(1)C_6Cl_4(2)CO_2K$	From tetrachlorfluorescein.
Gallein. Alizarin Violet. Anthracene Violet.	$C-(1)C_6H_2\begin{cases}(4)O\\(5)O\end{cases}>$ $\begin{cases}(6)\\(6)\end{cases}>O$ $(1)C_6H_2\begin{cases}(4)OH\\(5)OH\end{cases}$ $(1)C_6H_4(2)CO.O$	From gallic acid and phthalic anhydride.
Cœrulein. Alizarin Green. Anthracene Green.	$C-(1)C_6H_2\begin{cases}(4)O\\(5)OH\end{cases}$ $\begin{cases}(6)\\(6)\end{cases}>O$ $(1)C_6H\begin{cases}(5)O\\(4)O\end{cases}>$ $(1)C_6H_4(2)\overset{(2)}{>}CO$	From gallein.
Cœrulein S, and SW.	Sodium bisulphite compound of preceding.	From Cœrulein.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARAC- TERISTICS.
	With Caustic Soda.	With Hy- drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; brown solu- tion, green fluorescence.	Darker.	Yellow ppt.	Yellow.	Yellow ppt.	. . .
Brown powder; yellow solu- tion, strong green fluor- escence.	Darker.	Yellow ppt.	Yellow.	Yellow.	Soluble in alco- hol.
Brown powder; red solution, no fluor- escence.	No change.	Yellow ppt.	Yellow.	Yellow ppt.	. . .
Brown powder; red solution.	No change.	Precipitate.	Orange.	. . .	. . .
Red powder; bluish-red solution, green fluorescence.	No change.	Red ppt.	Yellow.	Orange ppt.	Soluble in alco- hol.
Red powder; bluish-red solution.	No change.	Pink ppt.	Brown.	Pink ppt.	. . .
Violet paste or green powder; red solution.	Blue.	Brown.	Orange.	No change.	Soluble in alco- hol.
Black paste; in- soluble.	Green.	No change.	Brown.	Black ppt.	. . .
Black powder; brown solu- tion.	Green ppt.	No change.	Brown.	Black ppt.	Soluble in hot al- cohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Rhodamine B.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)N(C_2H_5)_2\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N(Cl)(C_2H_5)_2\end{cases}\\(1)C_6H_4(2)CO_2H\end{cases}$	From phthalic anhydride.
Rhodamine S.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)N(CH_3)_2\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N(Cl)(CH_3)_2\end{cases}\\C_2H_4.CO_2H\end{cases}$	From tetra-chlorfluorescein.
Rhodamine G.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_2H_5\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N(Cl)(C_2H_5)_2\end{cases}\\(1)C_6H_4(2)CO_2H\end{cases}$	From rhodamine B.
Rhodamine 6 G.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_2H_5\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)NH.C_2H_5\end{cases}\\(1)C_6H_4(2)CO_2.C_2H_5\end{cases}$	From diethyl-rhodamine.
Rhodamine 3 B.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)N(C_2H_5)_2\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N(Cl)(C_2H_5)_2\end{cases}\\(1)C_6H_4(2)CO_2.C_2H_5\end{cases}$	From tetra-ethyl-rhodamine.
Violamin B.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_6H_4.SO_3Na\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N.C_6H_5\end{cases}\\(1)C_6H_4(2)CO_2H\end{cases}$	From fluoresceïn chloride.
Violamin R.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_6H_3\begin{cases}CH_3\\SO_3Na\end{cases}\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N.C_6H_4.CH_3\end{cases}\\(1)C_6H_4(2)CO_2H\end{cases}$	From fluoresceïn chloride.
Violamin G.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_6H\begin{cases}(CH_3)_3\\SO_3Na\end{cases}\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N.C_6H_2(CH_3)_3\end{cases}\\(1)C_6H_4(2)CO_2H\end{cases}$	From fluoresceïn chloride.
Violamin 2 R.	$C=\begin{cases}(1)C_6H_3\begin{cases}(4)NH.C_6H_3\begin{cases}O.C_2H_5\\SO_3Na\end{cases}\\(6)\\(6)\end{cases}>O\\(1)C_6H_3\begin{cases}(6)\\(4)N.C_6H_4.OC_2H_5\end{cases}\\(1)C_6H_4Cl_2.CO_2H\end{cases}$	From dichlorfluoresceïn chloride.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Green crystals; bluish-red solution with strong fluorescence.	Red ppt.	Green ppt. soluble in excess.	Brown.	Bluish-red.	Soluble in alcohol.
Crystalline powder; red solution with yellow fluorescence.	Decolorized.	. .	Yellow.	Red.	. . .
Orange powder; violet solution, with fluorescence.	On heating decolorized and ppt.	Yellow.	Yellow.	Fluorescent.	Soluble in alcohol.
Brown powder; red solution, with green fluorescence.	Red ppt.	Red ppt.	Yellow.	Red.	Soluble in alcohol.
Red powder; red solution with fluorescence.	Red ppt. on heating.	Yellow.	Yellow.	Red.	Soluble in alcohol.
Violet powder; violet solution.	No change.	Blue ppt.	Orange.	Blue ppt.	Soluble in alcohol.
Red powder; red solution.	No change.	Violet ppt.	Orange.	Violet ppt.	Soluble in alcohol.
Red powder; red solution.	Yellow.	Red ppt.	Yellow.	Red ppt.	Soluble in alcohol.
Violet powder; blue solution.	Violet.	Blue ppt.	Red.	Blue ppt.	Soluble in alcohol.

Phthaleïns from Amidophenols.

Several coloring matters have appeared in commerce which are obtained by the reaction of phthalic anhydride on amidophenols or their allies. The representative member of this group of bodies is:—

$$\text{Rhodamine, } C_6H_4 \left\{ \begin{array}{l} CO.C_6H_3 \\ CO.C_6H_3 \end{array} \right. \left\{ \begin{array}{l} N(C_2H_5)_2 \\ O \\ N(C_2H_5)_2 \end{array} \right. \qquad \text{This} \qquad \text{body} \qquad \text{is}$$
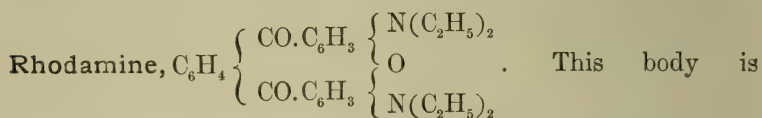
formed by heating, for several hours at 200°, one molecule of phthalic anhydride with two of diethyl-meta-amidophenol. The commercial product is a hydrochloride of the base, and forms a red powder, readily soluble in water with fine crimson color and a characteristic yellow fluorescence, which disappears on heating the solution to about 90° and is restored on cooling. Acids turn the color of the liquid somewhat yellower, and alkalies slightly bluer. Tannic acid, in presence of sodium acetate, gives a bright crimson precipitate of rhodamine tannate which is not fast to light, but if tartar-emetic be also present the compound precipitate formed resists light very well. With stannous chloride, an aqueous solution of rhodamine gives a characteristic cinnabar-red precipitate, which, while still in a fine state of division, transmits a bright blue light (E. K n e c h t, *Jour. Soc. Dyers, &c.*, iv. 96). In strong sulphuric acid, rhodamine dissolves with yellow color, changing to red on dilution with water. Rhodamine dyes silk and wool a pink color, with a marked orange fluorescence. The dye stands light and soaping fairly well. It may be mordanted on cotton with turkey-red oil, or tannic acid and tartar-emetic. The colors obtained are fluorescent.

Rhodamine B is the basic hydrochloride of diethyl-meta-amido-phenolphthaleïn. It is also called *Rhodamine O* and *Safranilin*. *Rhodamine S* is the succineïn of dimethyl-meta-amido-phenol, and is prepared by heating succinic anhydride with dimethyl-meta-amidophenol. It is used chiefly for coloring paper-pulp and wood. *Rhodamine G* is probably tri-ethyl rhodamine, and is prepared by heating rhodamine B with aniline hydrochloride. *Rhodamine 6G* is the ethyl ester of diethylrhodamine. *Rhodamine 3B* or *Anisoline* is the ethyl esther of tetra-ethyl rhodamine. There is another class of amido-phenol-phthaleïns, somewhat analogous to the preceding rhodamines. They are known by the general name

of *violamins;* they are in general tolyl-amidophenolphthaleïns. *Violamin B* or *Fast Acid Violet B* is the sodium sulphonate of diphenyl-meta-amidophenolphthaleïn, and is prepared by the action of paratoluidine on fluoresceïn chloride. *Violamin R* or *Fast Acid Violet A2R* is the sodium sulphonate of diorthotolyl-meta-amidophenolphthaleïn, and is prepared from orthotoluidine in the same manner as the preceding. *Violamin G* or *Acid Rosamin A* is the sodium sulphonate of dimesityl-meta-amidophenolphthaleïn. *Violamin 2R* or *Fast Acid Blue R* is a derivative from amido-dichlorphenolphthaleïn.

7. Indophenols.

The indophenols, together with the following groups—the oxazines, thiazines, and azines—are all somewhat closely related both in their chemical constitution and in derivation. They have previously been included under the general heading of *safranines,* but for reasons of systematic classification, it has been thought advisable to separate them into the above-named grouping.

A general method for the production of indophenols consists in the oxidation of a paradiamido-base in the presence of a phenol. The chief member of the class is prepared by reducing nitrosodimethyl-aniline in aqueous solution to dimethyl-paraphenylenediamine, $NH_2.C_6H_4.N(CH_3)_2$, filtering, and treating the filtrate with a solution of two molecules of alpha-naphthol in caustic soda. Potassium bichromate is next added, and then acetic acid till the liquid acquires an acid reaction, when the coloring matter is precipitated. Indophenol may also be obtained by the direct action of nitro-dimethylaniline on alpha-naphthol.

INDOPHENOL or NAPHTHOL BLUE, $C_{18}H_{16}N_2O$, prepared as above, is a feeble base which probably has the constitution expressed by the formula:—
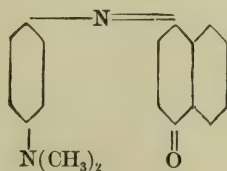
This is borne out by its reduction by stannous acetate to a l e u c o - b o d y possessing both acid and basic properties, and having the formula:—
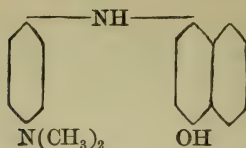
Commercial *indophenol N* forms a blue paste or dark brown powder, which when dry has a coppery reflection and closely resembles some varieties of indigo. When heated it sublimes in needles. Indophenol is quite insoluble in water, but dissolves in alcohol with a blue color, and in strong sulphuric acid with a dirty yellow-brown color, the solution giving a brown precipitate on dilution. The alcoholic solution is turned reddish-brown by hydrochloric acid, but is unchanged by alkalies. The alkaline solution, or the solid dye in presence of alkali, is decolorized by reducing agents, such as stannous chloride or glucose, so that a vat can be prepared from indophenol in the same way as from indigo.

REDUCED INDOPHENOL, or WHITE INDOPHENOL, $C_{18}H_{18}N_2O$, occurs in commerce as a yellowish-white paste, soluble in pure or acidulated water. It is unchanged by hydrochloric acid. In presence of an alkali and air it gradually oxidizes to blue indophenol, or immediately on cautious treatment with bichromate of potassium or a hypochlorite.

Indophenol is employed as a substitute for indigo in wool and cotton dyeing. It forms a lake with chromic oxide. On the fibre it is best recognized by being turned greyish-brown or dark grey by treatment with somewhat dilute (10 per cent.) hydrochloric acid, while indigo and other dark blue dyes are unaffected.

Indophenol may be applied as an ingrain color by impregnating the material with a mixture of the diamine and phenol, and subsequently developing the color by oxidation with potassium bichromate or bleaching powder. The colors obtained with indophenol are very fast to soap and light, but being very sensitive towards acids, prevents the substitution of indophenol for indigo.

8. Azines, Oxazines, and Thiazines.

The dyestuffs belonging to these classes contain the groupings:

Azines.   Oxazines.   Thiazines.
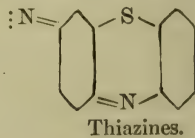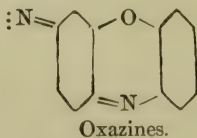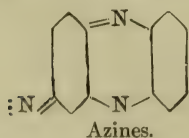
The azines may be subdivided into three classes:—(a) *Eurhodines*, (b) *Safranines*, (c) *Indulines.*

Eurhodines.

O. N. W i t t defines the e u r h o d i n e s as dye-stuffs which are derived from azines by the replacement of an atom of hydrogen by an amido-group, thus differing from the s a f r a n i n e s, which contain two amido-groups, and are the salts of a z o n i u m - b a s e s.

NEUTRAL VIOLET, $C_{14}H_{14}N_4,HCl$, is produced by the reaction of nitroso-dimethylaniline on meta-phenylenediamine. The commercial coloring matter is a greenish-black powder, the dust of which is intensely irritating to the mucous membrane. It dissolves easily in water with violet-red color. The solution is scarcely changed by a little hydrochloric acid, but is turned blue by excess. Soda produces a brown precipitate. In concentrated sulphuric acid the dye dissolves with a green (or, according to Zetter, a dirty violet) color, which on adding water becomes blue, and on further dilution violet.

NEUTRAL RED or TOLUYLENE RED, $C_{15}H_{16}N_4,HCl$, is homologous with the last color. It forms a greenish-black powder easily soluble in water with a bluish-red color, which turns bluer and then disappears on warming with zinc and hydrochloric acid, but returns on exposing the reduced solution to the air. In alcohol the dye dissolves to a magenta-red solution, which exhibits a strong brownish-red fluorescence. With hydrochloric acid the aqueous solution becomes bluer, and with excess pure blue. With soda it yields a yellowish-brown pricipitate, soluble in ether with greenish-yellow fluorescence. In strong sulphuric acid, toluylene red dissolves with a bluish-green color, changing to blue and magenta-red on adding water.

Safranines. The dyes of this class all contain the group:—

$$:\left\{ \begin{array}{c} N \\ | \\ N \end{array} \right\}:$$
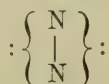
The two unsatisfied bonds are usually united to phenylene either substituted or intact, but in a few cases are satisfied by $C_{10}H_6$. In addition, one or both of the nitrogen atoms exercise pentavalent functions, as will be seen on reference to the foregoing table. This constitutes a distinction between the safranines and the e u r h o d i n e s, as in the latter both the nitrogen atoms appear to be trivalent.

A general method for the production of the safranines consists in the oxidation of one molecule of a paradiamido-base with two molecules of a mono-amido-base in a hot, neutral, aqueous solution.[1] Potassium bichromate is a suitable oxidizing agent. The simplest member of the class, namely, p h e n o s a f r a n i n e, is obtained by oxidizing a mixture of paradiamido-benzene and aniline hydrochloride, $C_6H_8N_2 + 2C_6H_7N + 2O_2 = C_{18}H_{14}N_4 + 4H_2O$.

The safranines of commerce are the chlorides of compound ammonium bases called a z o n i u m s. The free bases are but little known. Their salts, which usually crystallize well, are red or violet dyes, the dilute aqueous solutions of which give no precipitate with alkalies. On treatment with deoxidizing agents they are reduced to colorless l e u c o s a f r a n i n e s, which readily absorb oxygen from the air, with re-formation of the original coloring matters.

The safranines mostly dissolve in strong sulphuric acid with a fine green color. On gradually adding water, the color of the liquid changes first to bluish-green, and then to a pure blue. With still more water, the solution becomes violet-blue, and ultimately acquires the color of an aqueous solution of the dye under examination. The green solution absorbs the violet, blue, and red rays of the spectrum, and the bluish-green behaves similarly, but absorbs the red less perfectly; the blue solution absorbs only yellow light; and as by dilution the color changes to violet and red, the region of absorption approaches the green.

Safranine, *Safranine T, Safranine extra G,*[2] or *Aniline Pink.* This coloring matter, as it occurs in commerce, is a mixture of several homologous bodies, of which $C_{19}H_{17}N_4Cl$, $C_{20}H_{19}N_4Cl$, and $C_{21}H_{21}N_4Cl$ are the chief. Safranine can be obtained by various methods, including the oxidation of m a u v e i n e, $C_{27}H_{25}N_4Cl$; the treatment of aniline with glacial acetic acid and lead nitrate; and by heating amido-azotoluene with toluidine nitrate. These methods are obsolete, that now employed being usually the oxidation of a mixture of aniline, ortho-toluidine and para-toluylene-

[1] Safranines are also formed when one molecule of meta- or para-toluidine, or of methyl- or dimethyl-aniline, is substituted for one of aniline. Both molecules of aniline may be similarly substituted by metatoluidine, but with two molecules of paratoluidine or of methyl- or dimethyl-aniline the formation of the coloring matter does not take place.

[2] Also known as: *Safranine S, Safranine GGS, Safranine GOOO, Safranine FF, Safranine AG* and *AGT extra.*

diamine in molecular proportions. Aniline oil of suitable composition is first converted into the amido-azo-compounds amido-azobenzene and amido-azotoluene. When reduced with zinc and hydrochloric acid, the first of these splits into aniline and para-phenylene-diamine, and the latter into ortho-toluidine and paratoluylene-diamine; thus—

$$C_6H_4(CH_3).N_2.C_6H_3(CH_3).NH_2 + 2H_2 = C_6H_4(CH_3).NH_2 + NH_2.C_6H_3(CH_3).NH_2.$$
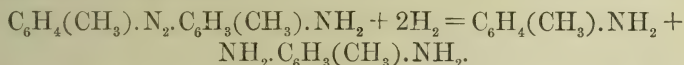
When the reaction is complete the liquid is diluted, a molecular proportion of toluidine hydrochloride added, and the mixture oxidized by potassium bichromate. The product is boiled with milk of lime, and the liquid filtered, neutralized with hydrochloric acid, and saturated with salt. The precipitate is purified by solution in water, and again salted out.

Commercial safranine usually occurs as a reddish-brown powder, but the pure hydrochloride forms reddish crystals, soluble in water and alcohol. The alcoholic solution exhibits a fine yellowish-red fluorescence. Caustic alkalies and ammonia change the color of an aqueous solution of safranine to brownish-red, but no precipitate is produced unless the liquid is concentrated. The base is best prepared by treating a solution of the hydrochloride with argentic oxide, filtering, and evaporating the filtrate to dryness.

Safranine is one of the few coloring matters which are taken up by animal fibres from alkaline solutions. In alkaline or neutral solution safranine also possesses some affinity for cotton, but the color produced is not fast. The best mordant is tannin and tartar-emetic.

On the fibre, safranine is distinguished by being unchanged by dilute acid, but turned from red to blue-violet by concentrated hydrochloric acid. Ammonia and caustic soda remove the coloring matter without much previous change of tint. The color is bleached on warming the fibre with hydrochloric acid and stannous chloride. Alcohol strips fibres dyed with safranine, forming a red solution which exhibits a reddish-yellow fluorescence.

Magdala Red. NAPHTHALENE RED.[1] $C_{30}H_{21}N_4Cl + H_2O$. This coloring matter is prepared by heating a-naphthylamine in acetic acid solution to 150° with a molecular proportion of alpha-amido-azonaphthalene (prepared by diazotizing alpha-naphthylamine

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[1] Also known as: *Naphthalene Rose, Naphthalene Scarlet, Sudan Red, Rosa-naphthylamine,* and *Fast Pink* for silk.

hydrochloride). The melt is boiled with a large excess of hydrochloric acid, and the liquid filtered. The filtrate is neutralized, and salt gradually added, when the rosanaphthylamine is precipitated as a sparingly soluble hydrochloride, and a violet coloring matter and excess of naphthylamine remain in solution.

Naphthalene red is characterized by its very sparing solubility in water, even when hot, and by forming a cherry-red alcoholic solution, which exhibits a fluorescence of a remarkable cinnabar-red color. This behavior is simulated only by an alkaline solution of azoresorufin; but that substance differs from naphthalene red in the color it dyes silk, and in yielding a brown precipitate on addition of a strong acid. The fluorescence of a solution of naphthalene red is destroyed by ammonia or soda.

Magdala red is employed for producing a fluorescent pink on silk and velvet. It is not used on wool. Neither the shade nor fluorescence is altered in artificial light. It is distinguished from *eosin* by not being stripped from the fibre by alcohol, and by not being readily affected by alkalies or dilute acids.

Mauveine, $C_{27}H_{24}N_4$, is of interest as being the base of *Perkin's purple, aniline violet,* or *mauve,*[1] the first commercial dye from aniline. The free base may be obtained by adding caustic alkali to a boiling alcoholic solution of the crystallized acetate. It then separates as a black glistening powder, which is almost insoluble in ether or benzene, but in alcohol forms a violet solution, which is turned purple on adding a dilute acid, or even by carbonic acid. Mauveine is a strong base, decomposing ammonium salts and forming a carbonate.

Commercial mauve is usually a s u l p h a t e of the base. It is now almost obsolete, but occasionally occurs as a reddish-violet paste, sparingly soluble in hot water with violet-red color. The solution is unchanged by hydrochloric acid, but yields a bluish-violet precipitate with soda, and dyes silk a reddish-violet. In an excess of strong sulphuric acid, mauve dissolves with olive-green color, changing on adding water to green, sky-blue, and finally to a reddish-violet.

GIROFLÉ,[2] $C_{24}H_{27}N_4Cl$, is obtained by the action of nitrosodimethylaniline on a mixture of metaxylidine and paraxylidine.

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[1] Also known as: *Rosolane, Chrome Violet, Violeïn, Indisin, Phenamin, Purpurin, Tyralin, Tyrian Purple,* and *Lydin.*

[2] Also known as: *Tannin Heliotrope, Heliotrope B,* and *2B.*

Dyed on cotton it produces a red-violet shade, and is chiefly employed for shading alizarin reds and violets in calico-printing.

Indulines.

These bodies are very similar to the safranines, being derivatives of phenazine. They are produced by the reaction of amido-azo-compounds on the hydrochlorides of aromatic amines (*e. g.*, aniline), with elimination of ammonia. The substances of the induline class occurring in commerce are dark-blue or violet dyes, less remarkable for their brilliancy than their resistance to light and atmospheric influences.[1]

VIOLANILINE, $C_{18}H_{15}N_3$, the typical member of the class, is a base contained in the commercial coloring matters known as *nigrosine* and *induline*. It is a product of the oxidation of aniline ($C_6H_7N + O_3 = C_{18}H_{15}N_3 + 3H_2O$), and may be prepared by heating aniline with nitrobenzene and iron filings to 180° C. Violaniline is often present in magenta-residues, from which it may be prepared by boiling with hydrochloric acid, which dissolves the other bases,

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[1] The safranines, mauveïnes, indazines, and rosindulines all belong to the class of para-quinones; they all react with bases to form indulines—the formula of the simplest one being:
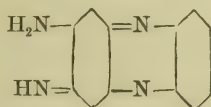
The safranines are distinguished from the indulines by their characteristic behavior with sulphuric acid. The simple safranines, aposafranine, phenosafranine, mauveïne, indazine, and rosinduline, dissolve in concentrated sulphuric acid with a green color, whilst the anilides dissolve to violet or blue solutions. Recognizing the relationship between the safranines and indulines, it is no longer necessary to insist on the old ammonium formula for the safranine salts, and Kehrmann's view (Ber. 28, 1710) that the salts of the induline bases and indones (rosinduline, etc.) are derived from an *o*-quinonoid azonium formula, whilst the oxygen-free induline bases and the indones are only *p*-quinonoid anhydrides of amido or of hydroxy-azonium bases, is untenable. It is more probable that the strong basicity of many of these color bases is due to the imido group, and not to the azine nitrogen. Hence aposafranine hydrochloride has probably the formula—
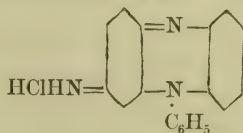
(*O. Fischer* and *E. Hepp, Ber.* xxix, 361.)

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and leaves violaniline hydrochloride and resinous matters undissolved. On treating these with boiling aniline, and filtering, the pure coloring matter separates out on cooling. The h y d r o c h l o r i d e so obtained is a bluish-black amorphous powder, insoluble in water but soluble in alcohol with bluish-violet color. The free base is precipitated in flakes on adding an alkali to this solution.

By heating violaniline with aniline, or by using excess of aniline in its manufacture, phenylated substitution-products are obtained, the highest of which is t r i p h e n y l - v i o l a n i l i n e, $C_{18}H_{12}(C_6H_5)_3N_3$.

By increasing the proportion of aniline hydrochloride, a series of indulines are obtained, the identity of which is determined by the proportions of the reagents and the temperature employed.

If two parts of diazo-amidobenzene, one of aniline hydrochloride, and four of aniline be mixed and allowed to stand for twenty-four hours, to allow of the conversion of the diazo-amido-azobenzene into the metameric body amido-azobenzene, and the mixture be then heated to 125°–130°, a more complex reaction ensues,[1] and a base is produced, the hydrochloride of which crystallizes from the liquid on cooling. The free base has the formula $C_{30}H_{23}N_5$, and forms warty crystals, soluble in alcohol with dark purple color. The h y d r o c h l o r i d e is the *induline 3 B* of commerce, and forms brownish shining scales, soluble with purple color in aniline or alcohol, and is used for producing delicate fast greys on cotton, for which fibre it has some little affinity.

By increasing the proportion of aniline hydrochloride in the melt, and raising the temperature to 165°–170° C., a base is obtained of the formula $C_{30}H_{22}(C_6H_5)N_5$, which crystallizes from aniline in needles having a green metallic reflection. The h y d r o c h l o r i d e, $C_{36}H_{27}N_5$, HCl, is the *induline 6 B* of commerce, and forms green lustrous crystals which readily lose hydrochloric acid.

The characters and reactions of the various commercial indulines are not strictly identical, but do not require separate description. As a class, the indulines usually occur as bluish-black or brownish-black powders, which are insoluble in water but soluble in alcohol

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[1] If the temperature be limited to 100°, the product consists largely of a z o - p h e n i n e, $C_{36}H_{29}N_5$, a base which crystallizes from hot aniline in small, garnet-red plates, melting at 236°, and forming a violet solution in strong sulphuric acid which becomes azure-blue at 300°, and exhibits a carmine-red fluorescence on dilution with water.

with greenish or bluish-violet color. The alcoholic solution becomes pure blue with hydrochloric acid, and on adding soda yields a dirty-red or reddish-violet solution or precipitate, the exact reaction depending on the nature of dye under examination.

SULPHONATED INDULINES. SOLUBLE INDULINES. By treating the indulines with strong sulphuric acid, various sulphonated indulines are obtained which are soluble in water. The redder shades are met with in commerce under the name of *fast blue R* and *water-soluble nigrosine*, and the bluer varieties as *fast blue B*, *fast blue greenish*, *induline 3 B* or *6 B*, etc. These sulphonated indulines occur as crystalline powders with a bronze reflection ("induline"), or as black, glistening fragments ("nigrosine"). They dissolve in water with bluish-violet, and in alcohol with blue color. Hydrochloric acid renders the solution blue. Alkalies produce a brownish-violet precipitate. In sulphuric acid, the sulphonated indulines dissolve with blue color, changing to violet on dilution with water. By oxidation they yield q u i n o n e and other products, and by reducing agents are converted into unstable leuco-derivatives.

Soluble indulines are used for the preparation of colored inks, and both the soluble and insoluble in the preparation of spirit-varnishes. They are very fast dyes, and are employed for producing grey, bluish, and blue-black shades on wool, silk, leather, etc., and are used as indigo-substitutes. In commerce they are met with under a variety of names, including, besides those already mentioned, *Blackley blue*, *Guernsey blue*, *indigo-substitute*, *bengaline*, *Coupier's blue*, *acetin blue*, *pelican blue*, *indigen D, F, sloeline, RS, BS, azine blue, indophenin extra, soluble blue CB, printing blue, printing blue H, R, B, Bengal blue, fast blue RR.*, etc.

On the fibre, the indulines are turned somewhat bluer by hydrochloric acid, but nitric acid is almost without action (distinction from indigo). Ammonia and soda strip the fibre, forming reddish-violet solutions, which are decolorized by zinc powder, but the color returns on filtering and exposing the liquid to the air. An acid solution of stannous chloride strips the fibre, and forms a green solution. Hypochlorites bleach some indulines, and turn others reddish-gray.

In the following table will be found the properties and reactions of the chief dyestuffs belonging to the azine group. The eurodines have been considered on page 333.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Safranin.	$\begin{matrix} CH_3(3) \\ NH.HCl(4) \end{matrix}\Big\} C_6H_2 \Big\{ \begin{matrix}(1)N(1)\\(6)N(6)\end{matrix} \Big\} C_6H_2 \Big\{ \begin{matrix}(3)CH_3\\(4)NH\end{matrix}$ $\underset{\displaystyle C_6H_5}{\mid}$	From mauveïne.
Magdala Red.	$C_{10}H_5 \left\{ \begin{matrix}(1)N\\(4)NH\\(2)N(2)\end{matrix} \right\} C_{10}H_6$ $\underset{\displaystyle C_{10}H_7}{\mid}$ (The base)	From a-napthyla-mine.
Mauve.	$\underset{\displaystyle HCl}{\overset{\displaystyle CH_3(3)}{C_6H_5.N(4)}}\Big\} C_6H_2 \Big\{ \begin{matrix}(1)N(1)\\(6)N(6)\end{matrix} \Big\} C_6H_2 \Big\{ \begin{matrix}(3)CH_3\\(4)NH_2\end{matrix}$ $\underset{\displaystyle C_7H_7}{\mid}$	From aniline.
Neutral Blue.	$(CH_3)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_{10}H_6$ $\underset{\displaystyle C_6H_5}{\mid}$	· · ·
Azine Green GB, TO.	$(CH_3)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_{10}H_5(6)NH.C_6H_5$	· · ·
Basle Blue R and BB.	$(CH_3)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_{10}H_5(7)NH.C_6H_4.CH_3$ $\underset{\displaystyle C_6H_4.CH_3}{\mid}$	· · ·
Basle Blue S.	Sodium salt of a sulphonic acid of the above.	From Basle Blue.
Azine Green S.	Sodium salt of a sulphonic acid of Azine Green.	From Azine Green.
Safranine B. Phenosafra-nine.	$H_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_6H_3(4)NH_2$ $\underset{\displaystyle C_6H_5}{\mid}$	· · ·
Amethyst Violet.	$(C_2H_5)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_6H_3(4)N(C_2H_5)_2$ $\underset{\displaystyle C_6H_5}{\mid}$	· · ·
Giroflé.	$(CH_3)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} \Big\{ \begin{matrix}(3)CH_3\\(6)CH_3\\(4)NH_2\end{matrix}$ $\underset{\displaystyle C_6H_3(CH_3)_2}{\mid}$	· · ·
Fast Neutral Violet B.	$(CH_3)_2N(4)C_6H_3 \underset{\displaystyle \overset{\mid}{Cl}}{\Big\{} \begin{matrix}(1)N(1)\\(2)N(2)\end{matrix} \Big\} C_6H_3(4)NH.C_2H_5$ $\underset{\displaystyle C_2H_5}{\mid}$	· · ·

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Brown powder; red solution.	Red ppt.	Violet.	Green.	Blue to red.	Soluble in alcohol.
Brown powder; red solution in hot water.	Violet ppt.	Bluer.	Violet.	Red ppt.	Soluble in alcohol, with red fluorescence.
Violet paste; red solution in hot water.	Violet ppt.	No change.	Green.	Violet.	. . .
Brown powder; violet solution.	Violet ppt.	No change.	Violet.	Violet.	Soluble in alcohol.
Green powder; green solution.	Green ppt.	Green ppt.	Brown.	Green.	Soluble in alcohol.
Brown powder; violet solution.	. .	Blue ppt.	Brown.	Violet ppt.	. . .
Coppery powder; blue solution.	. .	. .	Yellow.	. .	. . .
Black powder; bluish-green solution.	No change.	No change.	Violet.	Green.	. . .
Green crystals; red solution.	Brown ppt.	Violet.	Green.	Red.	. . .
Gray powder; violet solution.	No change.	Blue.	Green.	Violet.	Soluble in alcohol. Obsolete.
Green powder or brown paste; red solution.	Red ppt.	No change.	Green.	Red.	Soluble in alcohol.
Bronze powder; violet solution.	No change.	No change.	Grey.	Violet.	Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Indazine NV.	$C_6H_5N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2$ $\mid$ $\dot{C}_6H_5$ and $\qquad$ (Bases.) $(CH_3)_2N.C_6H_4N(5)\Big\}C_6H_2\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2$ $\mid$ $\dot{C}_6H_5$	$\cdot\ \cdot$
Metaphenyl-ene Blue B.	$C_7H_7N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2$ $\mid$ $\dot{C}_7H_7$	$\cdot\ \cdot$
Methylene Violet RRA, 3 RA. Fuchsia.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)NH_2$ $\mid\qquad\qquad\mid$ $\dot{C}l\qquad\quad\ \dot{C}_6H_5$	$\cdot\ \cdot$
Safranin NN. Clementine.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(4)NH_2\\(5)CH_3\end{matrix}\right.$ $\mid\qquad\qquad\mid$ $\dot{C}l\qquad\quad\ \dot{C}_6H_5$	$\cdot\ \cdot$
Rosolan.	$C_6H_5N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3\left\{\begin{matrix}(4)NH_2\\(5)CH_3\end{matrix}\right.$ $\mid\qquad\qquad\mid$ $\dot{H}Cl\qquad\ \dot{C}_6H_5$	Of Farbwerke vorm. Lucius & Brünig.
Naphthazine Blue.	$C_{10}H_7N(4)C_6H_3\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2$ $\mid$ $\dot{C}_{10}H_7$ (Base.)	$\cdot\ \cdot$
Induline.	Has the following bases: $\left.\begin{matrix}C_6H_5HN(5)\\C_6H_5N\ (4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)NH_2$ $\mid$ $\dot{C}_6H_5$ $\left.\begin{matrix}C_6H_5HN(5)\\C_6H_5N\ (4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)NH.C_6H_5$ $\mid$ $\dot{C}_6H_5$ $\left.\begin{matrix}C_6H_5HN(5)\\C_6H_5N\ (4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(4)NH.C_6H_5\\(5)NH.C_6H_5\end{matrix}\right.$ $\mid$ $\dot{C}_6H_5$	From aniline.
Fast Blue R.	Consists of sodium salts of sulphonic acids of various indulines.	From indu-lines.
Paraphenyl-ene Blue R. Fast New Blue for Cotton.	Uncertain.	From amido-azo-benzene.
Toluylene Blue B, for cotton.	$NH_2.C_6H_2(CH_3)N(4)\Big\}C_6H_2\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(4)NH.C_6H_5$ $\mid$ $\dot{C}_6H_5$	From spirit in-duline.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Bronze powder; blue solution.	Blue ppt.	No change.	Green.	Blue.	Soluble in alcohol.
Dark powder; violet solution.	Violet ppt.	Bluer.	Gray.	Blue.	Soluble in alcohol.
Dark powder; violet solution.	Brown ppt.	Violet.	Green.	Violet.	Soluble in alcohol.
Metallic powder; violet solution.	Red ppt.	Blue.	Green.	Violet.	Soluble in alcohol.
Dark powder; violet solution.	Violet ppt.	No change.	Green.	Red.	Soluble in alcohol.
Bronze powder; blue solution.	Duller.	Bluer.	Green.	Blue.	. . .
Black powder; insoluble.	Violet ppt. (in alcoholic solution).	Blue (in alcoholic solution).	Blue.	Blue ppt.	Soluble in alcohol.
Bronze powder; violet solution.	Violet ppt.	Bluer.	Blue.	Violet.	Soluble in alcohol.
Dark powder; blue solution.	Violet ppt.	No change.	Blue.	No change.	Soluble in alcohol.
Violet powder; blue solution.	Brown ppt.	Precipitate.	Blue.	. .	. .

COMMERCIAL NAME.	FORMULA.	REMARKS.
Para Blue.	Uncertain.	An induline dye-stuff.
Milling Blue.	$C_6H_5N(4)C_{10}H_5 \left\{ \begin{matrix} (1)N(1) \\ (2)N(2) \end{matrix} \right\} C_{10}H_5(4)NH.C_6H_5$ $\underset{(Base.)}{\overset{\mid}{C_6H_5}}$	. . .
Paraphenylene Violet.	Uncertain.	From p-phenyl-ene-diamine.
Azindone Blue G.	Uncertain.	From indulines.
Azindone Blue R.	Uncertain.	From indulines.
Indamin GG.	Uncertain.	Induline derivative.
Indamin J and JO.	Uncertain.	Induline derivative.
Indamin R.	Uncertain.	Induline derivative.
Indamin 2 R and 3 R.	Uncertain.	Induline derivative.
Indamin 6 R.	Uncertain.	Induline derivative.
Indamin Blue N.	Uncertain.	Induline derivative.
Indamin Blue N extra.	Uncertain.	Induline derivative.
Indamin Blue NB.	Uncertain.	Induline derivative.
Indamin Blue NB extra.	Uncertain.	Induline derivative.
Indamin Blue WG.	Uncertain.	Induline derivative.
Indamin Blue NR.	Uncertain.	Induline derivative.
Indamin Vat Blue.	Uncertain.	Induline derivative.
Rubramin.	Uncertain.	Induline derivative.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Blue powder; blue solution.	Violet ppt.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.
Bronze powder; blue solution.	Darker.	Blue ppt.	Bluish-green.	Blue.	. . .
Violet powder; violet solution.	Violet ppt.	Redder.	Green.	. .	. . .
Violet powder; blue solution.	Violet ppt.	Redder.	Green.	Violet.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	Redder.	Green.	Violet.	Soluble in alcohol.
Gray powder; blue solution.	Precipitate.	No change.	Green.	Bluer.	Soluble in alcohol.
Red powder; blue solution.	Precipitate.	No change.	Green.	Turbid.	Soluble in alcohol.
Brown powder; blue solution.	Redder.	No change.	Green.	Violet.	Soluble in alcohol.
Gray powder; violet solution.	Violet ppt.	No change.	Green.	Red.	Soluble in alcohol.
Green powder; magenta - red solution.	Red ppt.	No change.	Green.	Red.	Soluble in alcohol.
Gray powder; blue solution.	Violet ppt.	Bluer.	Black.	Violet.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	Blue.	Bluish-green.	Violet.	Soluble in alcohol.
Brown powder; blue solution.	Redder.	Greener.	Green.	Blue.	Soluble in alcohol.
Coppery powder; blue solution.	Blue ppt.	No change.	Green.	Blue.	Soluble in alcohol.
Red powder; blue solution.	Redder.	Darker.	Green.	Blue.	Soluble in alcohol.
Gray powder; blue solution.	Violet.	No change.	Green.	Purple.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	Blue ppt.	Green.	Blue ppt.	Soluble in alcohol.
Green powder; cerise solution.	Red ppt.	No change.	Green.	Red.	Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Nigramin.	Uncertain.	Induline derivative.
Flavindulin.	$C_{14}H_8\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_4$ C_6H_5 Cl.	From phenanthra-quinone.
Induline Scarlet.	(Base :) $NH(4)C_{10}H_5\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_3(5)CH_3$ $\overset{\mid}{C_2H_5}$	. . .
Azocarmine G. Rosazin.	(Base :) $C_6H_5N(4)C_{10}H_5\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_4$ $\overset{\mid}{C_6H_5}$	Phenylrosindulin.
Azocarmine B. Rosindulin 2 B.	Di-sodium salt of phenylrosindulin tri-sulphonic acid.	. . .
Rosindulin 2 G.	(Base :) $O(4)C_{10}H_5\left\{\begin{matrix}(1)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_4$ $\overset{\mid}{C_6H_5}$	Sodium salt of the monosulphonic acid.
Rosindulin G.	$\left.\begin{matrix}NaO_3S(6)\\O(4)\end{matrix}\right\}C_{10}H_4\left\{\begin{matrix}(2)N(1)\\(2)N(2)\end{matrix}\right\}C_6H_4$ $\overset{\mid}{C_6H_5}$	. . .

Character of Dyestuff.	Reaction of Aqueous Solution.		Reaction of Dye with Sulphuric Acid.		Other Characteristics.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Black powder; violet solution.	Violet ppt.	No change.	Green.	Violet.	Soluble in alcohol.
Orange powder; orange solution.	Yellow ppt.	No change.	Violet.	Yellow.	. . .
Red powder; red solution.	Violet ppt.	No change.	Red.	Green to red.	Soluble in alcohol.
Red paste; bluish-red solution.	No change.	Red ppt.	Green.	Red ppt.	. . .
Brown powder; violet solution.	No change.	Brown ppt.	Green.	. . .	. . .
Scarlet powder; scarlet solution.	Scarlet ppt.	Yellow ppt.	Green.	Orange.	. . .
Red powder, red solution.	Scarlet ppt.	Yellow ppt.	Green.	. . .	. . .

Oxazines.

These coloring matters are produced by the action of phenoloids on a *salt* of nitroso-dimethylaniline or an allied body. All the oxazines contain the group:—

 or $\equiv N(4)C_6H_3 \left\{ \begin{matrix} (2)O(2) \\ (1)N(1) \end{matrix} \right\} C_6H_4$
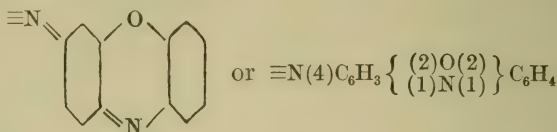
GALLOCYANIN DH and BS, or Fast Violet, $C_{15}H_{13}N_2O_5Cl$, occurs usually in commerce as a nearly insoluble, greenish-gray paste, which forms a bronze powder on drying. It is soluble in caustic soda with a deep violet color. It is produced by the action of nitroso-dimethylaniline hydrochloride on gallic acid. In its chemical nature it exhibits both basic and acid properties; with mineral acids it forms salts which are red, while with metallic bases the salts are bluish violet. Gallocyanin BS is the bisulphite compound of gallocyanin.

PRUNE, $C_{16}H_{15}N_2O_5Cl$, is the methyl ether of gallocyanin, and forms small bronze crystals or a dark brown powder. It is soluble in water and alcohol with bluish-violet color. Hydrochloric acid turns the solution magenta-red, and soda gives first a brown precipitate, and with excess of the reagent a violet solution. In concentrated sulphuric acid the dye dissolves with corn-flower blue color, changing to magenta-red on dilution.

MELDOLA'S BLUE, or NEW BLUE (Cassella),[1] $C_{18}H_{15}N_2OCl$, is produced by the reaction of betanaphthol on nitroso-dimethylaniline hydrochloride. It occurs in commerce as a dark violet powder with bronze reflection. The dust strongly irritates the mucous membrane. In water it is soluble with bluish-violet color; in alcohol with blue color. The violet aqueous solution becomes at first green and then colorless when reduced by zinc and acetic acid, the original color returning on exposure to air. The solution is turned blue by hydrochloric acid, and with soda yields a brown precipitate.[2] In strong sulphuric acid the dye dissolves with a

[1] Also known as: *New Blue R, New Fast Blue for Cotton, Naphthylene Blue R in crystals, Cotton Blue R for cotton, Cotton Blue R, Fast Marine Blue, Fast Cotton Blue R, RR, 3R, crystals; Phenylene Blue, Blue Nouveau P, Fast Blue III R, Fast Marine Blue RM, MM, Naphthol R and D.*

[2] If this precipitate is dissolved in sulphuric acid a group of dyestuffs called *Cyanimides* is obtained. They are coloring matters of a purple greenish-blue shade.

blackish-green color, becomes first blue and then violet on dilution. Naphthalene blue dyes cotton mordanted with tannin and tartar-emetic an indigo-blue color.

MUSCARIN, or CAMPANULIN, $C_{18}H_{15}N_2O_2Cl$, introduced by Durand and Haguenin, occurs in commerce as a brown-violet powder, sparingly soluble in cold but readily in hot water, with bluish-violet color. The solution is decolorized by heating with zinc-dust, but the color returns on exposure to air. Hydrochloric acid produces a bluish-violet and soda a yellowish-brown precipitate. Tannin precipitates the solution with an indigo-blue color. In concentrated sulphuric acid muscarin dissolves with a bluish-green color, the solution turning first blue and then violet on adding water, and on further dilution giving a violet precipitate.

NILE BLUE A is produced by the reaction of alpha-naphthylamine on the hydrochloride of nitroso-dimethyl-metamidophenol. It occurs in commerce both as the *chloride*, the formula of which has already been given, and as a *sulphate* of the composition $(C_{18}H_{16}N_3O)_2SO_4$. The *sulphate* forms a green crystalline powder with bronze reflection. It is sparingly soluble in cold water, but readily in warm, with a blue color. It is also soluble in alcohol. The warm concentrated aqueous solution yields with hydrochloric acid needles of the chloride, which appear violet by transmitted and green by reflected light. Addition of soda to the dilute solution (1:1000) produces a red precipitate, soluble in ether to a brown-orange solution, with dark green fluorescence. Tannin in presence of sodium acetate gives a prussian-blue precipitate, and stannous chloride a dark greenish-blue precipitate, and on warming the liquid exhibits a green fluorescence, with blue transmitted light. In concentrated sulphuric acid, the dye dissolves with a yellow or red-brown color, changing to green and blue on dilution. Wool is dyed directly by Nile blue, a red shade of blue, and cotton mordanted with tannin and tartar-emetic is dyed blue. The color is not fast to light, and is liable to bleed when milled with soap, but not with soda.

METAMINE BLUE B AND G (*New Blue B and G, Fast Blue 2B for Cotton, Fast Cotton Blue B, Fast Marine Blue GM,* and *Naphthol Blue B*), is a dyestuff similar to Meldola's Blue, from which it is produced by condensation with dimethyl-paraphenylenediamine. It is dyed on cotton mordanted with tannin and tartar emetic.

CAPRI BLUE GN, is the zinc chloride double salt of dimethyl-phenyl-ammonium-dimethylamidotolyl-oxazine, and is obtained

by the action of nitroso-dimethylaniline on dimethyl-meta-amido-cresol. It occurs as green crystals which are soluble in water with a blue color. The addition of caustic soda yields a blue precipitate which gives a red solution in ether, possessing a red fluorescence. Dissolved in concentrated sulphuric acid the solution exhibits a dichroïc effect; in thin layers it appears green, in thick layers red, while by transmitted gaslight it appears crimson. It dyes cotton a greenish-blue on a mordant of tannin and tartar emetic, the shade being quite fast to light, soap, acids, and alkalies. It is also dyed on silk, giving a beautiful sea-green shade in artificial light.

DELPHIN BLUE or CRUMPSALL FAST BLUE, is the ammonium salt of dimethyl-phenylammonium-hydroxydioxyphenoxazin-phenyl-amine-sulphonic acid, and is obtained by the action of gallocyanin on aniline. The dyestuff occurs in commerce as the free sulphonic acid in the form of a dark paste, or as the ammonium salt in the form of a dark brown powder soluble in water. Delphin Blue is dyed on wool with the aid of a chromium mordant yielding dull blue shades very fast to light and fulling. It is dyed on cotton in a manner similar to gallocyanin.

AZORESORUFIN, $C_{24}H_{16}N_2O_7$,[1] is a substance which crystallizes from hot hydrochloric acid in small, garnet-red prisms. It is nearly insoluble in water and alcohol. In strong sulphuric acid, azoresorufin dissolves with bluish-violet color; with alkalies, particularly in alcoholic solution, it forms a carmine-red liquid with a splendid cinnabar-red fluorescence. This color is so intense that azoresorufin may be used as a delicate reagent for alkalies, 0.000004 gramme of caustic soda being sufficient to produce the reaction. Its extreme sensitiveness to alkalies renders azo-resorufin unsuitable for dyeing, but this objection does not extend to its b r o m o - d e r i v a t i v e.

Hexabrom-azoresorufin (?) is produced by adding bromine to a solution of azoresorufin in caustic alkali. On acidulating the solution with hydrochloric acid the coloring matter is precipitated, and may be purified by crystallization from toluene. It may be

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[1] Azoresorufin was formerly called d i a z o - r e s o r u f i n, a name which suggests, without warrant, that it contains the d i a z o - g r o u p—N:N—; whereas its true constitution is probably expressed by the formula :—

$$C_6H_4 : \left\{ \begin{matrix} O \\ O \end{matrix} \right\} : N.C_6H_3 \left\{ \begin{matrix} OH \\ O \end{matrix} \right.$$
$$C_6H_4 : \left\{ \begin{matrix} O \\ O \end{matrix} \right\} : N.C_6H_3 \left\{ \begin{matrix} \\ OH \end{matrix} \right.$$
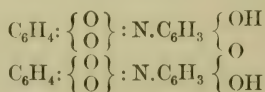
converted into the s o d i u m or a m m o n i u m s a l t, the latter of which constitutes the coloring matter known as

FLUORESCENT RESORCIN BLUE, or *Bleu fluorescent*. This dye stuff crystallizes in green lustrous needles, which are but slightly soluble in water or strong alcohol, but more readily in proof-spirit. The solutions are blue by transmitted and red by reflected light, and give a brown precipitate of hexabromresorufin on addition of a strong acid.

Fluorescent blue occurs in commerce as a 10 per cent. paste in which beetle-green crystals of the coloring matter may be recognized. It readily dyes silk in a neutral soap bath, the color produced being blue, with a slight admixture of red and gray, and a characteristic red fluorescence, easily visible in artificial light. It is perfectly fast to light, washing, and acids, but ammonia and soda strip the fibre, forming blue solutions with strong red fluorescence. Strong hydrochloric acid changes the color of fibres dyed with resorcin blue to brown.

Lacmoid Another blue coloring matter, sometimes called " resorcin-blue," can be obtained by slowly heating together 100 parts of resorcinol, 5 of sodium nitrite, and 5 of water. At 110° C. a vigorous reaction occurs, ammonia is evolved, and the mixture becomes red; when the melt is further heated to 115°–120° till the evolution of ammonia ceases, and the color changes to blue. The mass is then dissolved in water and the solution filtered and precipitated by hydrochloric acid. The product is a glistening brown powder, which is insoluble in chloroform, benzene, or petroleum spirit, easily soluble in alcohol, wood spirit, and amylic alcohol, and less soluble in water and ether. The coloring matter was named by its discoverers (T r a u b and H o c k, *Jour. Soc. Chem. Ind.*, iv. 297) l a c m o i d, owing to its behaving to acids and alkalies in a manner analogous to litmus, with the coloring matter of which they suggested it might be identical. R. T. T h o m s o n, however, has shown (*Chem. News*, lii., 18 and 31) that well-marked differences exist, lacmoid being far less sensitive to weak acids than is the case with litmus. In this respect lacmoid resembles helianthin (methyl-orange), for which it may be substituted with advantage in certain cases. Thus it is superior to all other indicators for determining the carbonates of the earthmetals (temporary hardness of water, *Chem. News*, xlix. 34). In most cases, lacmoid paper is preferable to the solution, which when used should be made with proof-spirit and of 5 per cent. strength.

Lacmoid paper can be employed in cases where the dark color of the liquid renders methyl-orange unsuitable. Thus, bichromate of potassium, $K_2Cr_2O_7$, and the corresponding salt of sodium are exactly neutral to lacmoid, the chromates of neutral constitution, M_2CrO_4, being strongly alkaline in reaction. An admixture of 1 per cent. of K_2CrO_4 can be detected and estimated in $K_2Cr_2O_7$ by means of lacmoid paper, if, after immersion, the paper be washed to remove the strongly colored liquid. The bodies represented by the following formulæ are also neutral to lacmoid:— $FeSO_4$, $FeCl_2$, $CuSO_4$, $CuCl_2$, $ZnSO_4$, H_3BO_3, H_3AsO_3, KH_2AsO_4, NaH_2PO_4, $NaHSO_3$. (Compare helianthin, phenolphthaleïn, congored and litmus.)

Thiazines.

When the aromatic diamines are heated with sulphur, sulphuretted bases are formed, which yield violet coloring matters on oxidation. These bodies may be obtained more simply by passing sulphuretted hydrogen through the solution of the hydrochloride of the diamine, and then adding ferric chloride. These dyestuffs possess a chemical constitution analogous to the oxazines, the atom of oxygen in the latter being replaced by one of sulphur. Hence the formula of this group corresponds to the following:

or $\equiv N(4)C_6H_3 \left\{ \begin{matrix} (1)S\,(2) \\ (2)N\,(1) \end{matrix} \right\} C_6H_4$
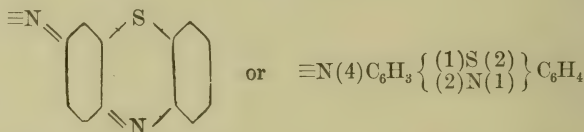
LAUTH'S VIOLET. $C_{12}H_{10}N_3SCl$. This curious coloring matter is the hydrochloride of the base t h i o n i n e. It crystallizes from a faintly acid solution in thin prismatic needles, having a beetle-green lustre. It dissolves slightly in cold but more readily in hot water, to form a solution which appears violet-red by transmitted, and violet-blue by reflected light. It is almost entirely precipitated from its aqueous solution by strong hydrochloric acid, but on adding excess redissolves with fine dark blue coloration. By precipitating a solution of Lauth's violet with soda or ammonia, the free b a s e, $C_{12}H_9N_3S$, may be obtained as a brownish-red or black crystalline precipitate, or from a hot solution in small needles with a feeble green reflection. Thionine dissolves only slightly even in hot water, but more readily in alcohol, to a red-

dish-violet solution, which exhibits a fine brownish-red fluorescence.

Thionine and its salts dissolve in strong sulphuric acid with fine yellowish-green color, changing to blue and violet on dilution with water. In this reaction thionine exactly resembles the safranines.

Lauth's violet is not employed in practice, but the important coloring matter known as *methylene blue* has the constitution of a t e t r a m e t h y l - t h i o n i n e h y d r o c h l o r i d e.

Methylene Blue.[1] $C_{16}H_{18}N_3SCl$. This coloring matter may be represented by the following formula:—

$$(CH_3)_2N(4).C_6H_3 \left\{ \begin{matrix} (1)\overset{|}{N}(1) \\ (2)S(2) \end{matrix} \right\} C_6H_3.(4)\underset{Cl}{\overset{|}{N}}(CH_3)_2$$
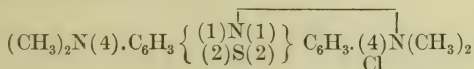
It may be prepared by treating dimethyl-aniline hydrochloride with sodium nitrite, and then with sulphuretted hydrogen until the solution loses its yellow color and is covered with a blue scum, when ferric chloride or bichromate of potassium is added till the smell of sulphuretted hydrogen has disappeared. The liquid is then saturated with common salt and zinc chloride added. The precipitate is separated, redissolved in water, and again precipitated with salt and chloride of zinc. The product so obtained is the *double zinc salt.* From it the chloride may be prepared by adding strong hydrochloric acid to the concentrated solution. Methylene blue may also be obtained from helianthin and by various other reactions.

Methylene blue occurs in commerce as a hydrochloride, but more frequently as the d o u b l e z i n c s a l t. It forms a dark blue or reddish-brown powder with a bronze reflection. In water or alcohol it dissolves easily with a blue color. The solution is unchanged or turned greenish by hydrochloric acid. Caustic soda changes the color to violet, and the addition of strong alkali to a concentrated solution produces a dirty blue or violet-black precipitate. In concentrated sulphuric acid, methylene blue dissolves with a grass-green color, which, on addition of water, becomes first blue and then violet.

From a solution of commercial methylene blue, the i o d i d e,

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[1] Also known as: *Methylene Blue B, BG, and BB; Methylene Blue IaD and extra D; Ethylene Blue.* The latter is a mixture of methylene blue with methylene azure.

$C_{16}H_{18}N_3SI$, is completely precipitated on adding iodide of potassium, and potassium bichromate also completely precipitates the solution as a purple-violet c h r o m a t e.   Methylene blue forms a soluble compound with tannin which is taken up by metallic mordants.

Tetramethylthionine Hydroxide $C_{16}H_{18}N_3S.OH$, the free base of methylene blue, is most readily obtained by treating a solution of the iodide or chloride with freshly precipitated argentic oxide. On evaporating the filtered liquid *in vacuo*, the base is obtained as a dark amorphous mass which acquires a green metallic lustre when rubbed, forms a syrupy solution in water, and dissolves readily in alcohol.   The solution decomposes various metallic salts. like an alkali, but is very unstable.

By treating methylene blue with zinc and acetic acid, or with an alkaline solution of sodium hyposulphite, the l e u c o - d e r i v-a t i v e, $C_{16}H_{19}N_3S$, is obtained.   This body crystallizes from ether in flat satiny needles, having a penetrating odor resembling that of the lobster.   It is readily soluble in water, and is extremely oxidizable both in the dry state and in solution, methylene blue and other products being formed.   In acid solution, tetramethyl-leucothionine is more stable, and it forms a readily soluble and crystallizable double zinc salt.

The formation of methylene blue affords the most delicate and certain reaction for the detection of sulphuretted hydrogen in neutral or acid solution, far exceeding in this respect the reactions with lead salts and nitroprussides.   100 c.c. of the liquid to be tested should be treated with 2 c.c. of fuming hydrochloric acid, and a few grains of dimethyl-paradiamido-benzene sulphate added. On then adding a drop or two of ferric chloride solution, methylene blue will be formed either immediately or on standing, if any sulphuretted hydrogen was previously present.

Methylene blue is a valuable dye for cotton yarn and calico-printing.   The blue produced has a greenish shade, especially in artificial light.   The color is faster than aniline blue, being unaffected by light and unacted on by neutral soap solution or dilute hypochlorites.   Ammonia is also without action, but alkaline soaps and caustic alkalies remove the color.   On treating the fabric with hydrochloric acid, it is turned green and the dye is gradually removed, the acid liquid remaining green.   Stannous chloride and other reducing agents discharge methylene blue more rapidly than other blue dyes.   A three per cent. solution of potassium bichro-

mate changes a fabric dyed with methylene blue to violet, and finally discharges it. If the dye was mordanted with tannin, a dark brown color remains.

The behavior of methylene blue with reducing agents and the sensitiveness of the resultant leuco-derivative render the coloring matter of great value in bacteriological research. "The bacilli of tuberculosis, glanders, and cholera were first discovered by the aid of methylene blue." [1]

ETHYLENE BLUE closely resembles methylene blue, but is prepared by using diethyl-aniline instead of the lower homologue.

METHYLENE RED, $C_{16}H_{18}N_4S_4,2HCl$, is a secondary product obtained in the formation of methylene blue, especially if the treatment with sulphuretted hydrogen be too prolonged and much ferric chloride be used. It remains in the mother-liquor when the blue is precipitated by the addition of salt. It is decolorized by alkalies and reducing agents, and turned blue by oxidizing agents. A modified methylene blue is obtained from it in practice by treating the acid solution first with zinc-dust and then with ferric chloride.

METYHLENE GREEN is mononitro-methylene-blue, prepared by the action of nitrous acid on that dyestuff. It resembles methylene blue very closely in its properties, being dyed in the same manner. It gives bluish-green shades fast to light and soap.

THIONINE BLUE (*G and O extra*) is the zinc chloride double salt of trimethyl-ethylthionine. It occurs as a reddish-brown powder dissolving in water to a bluish solution. It dyes cotton on a tannin mordant.

[1] Methylene Blue (and the basic aniline colors in general) may be rendered soluble in benzene, carbon disulphide, etc., by converting them into their resinates or oleates. In the latter method the dye-stuff is precipitated by a soap solution, the resulting oleate filtered, dried, and then dissolved in the solvent. Or, the dry color may be dissolved in an alcoholic solution of oleic acid, the alcohol afterwards being distilled off, leaving the soluble oleate behind.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Oxazines. Azurin.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H_2 \left\{ {(4)CO_2H \atop (6)OH} \right\}$ $\overset{|}{Cl}$	. . .
Gallocyanin.	(Base:) $(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(3)OH \atop (4)OH \atop (6)CO} \right\}$ $\overset{|}{O}$	From gallic acid.
Prune.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(3)OH \atop (4)OH \atop (6)CO.OCH_3} \right\}$ $\overset{|}{Cl}$	From methyl ether of gallic acid.
Meldola's Blue.	$C_{10}H_6 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H_3(4)N(CH_3)_2 + ZnCl_2$ $\overset{|}{Cl}$	. . .
Muscarin.	$C_{10}H_5(OH) \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H_3(4)N(CH_3)_2$ $\overset{|}{Cl}$	. . .
Nile Blue	$(C_2H_5)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)O(1)} \right\} C_{10}H_5(4)NH_2$ $\overset{|}{\frac{1}{2}(SO_4)}$	. . .
Nile Blue 2 B.	$(C_2H_5)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_{10}H_5(4)NH.C_7H_7$ $\overset{|}{Cl}$	. . .
Metamine Blue B.	. . .	From Meldola's blue.
Capri Blue GN.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H_2 \left\{ {(4)N(CH_3)_2 \atop (5)CH_3} \right\}$ $\overset{|}{Cl}$	. . .
Delphin Blue.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(3)OH \atop (4)OH \atop (6)NH.C_6H_4.SO_3.NH_4} \right\}$ $\overset{|}{Cl}$	From gallocyanin.
Gallanilic Violet BS.	Uncertain.	. . .
Gallanilic Indigo P and PS.	Uncertain.	. . .
New Methylene Blue GG.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_{10}H_5(4)N(CH_3)_2$ $\overset{|}{Cl}$	From Meldola's blue.
Fast Black. Fast Blue Black.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H_2 \left\{ {(5)N(1) \atop (4)N(2)} \right\} C_6H_3(4)N(CH_3)_2$ $\overset{|}{Cl} \qquad \overset{|}{C_6H_5} \qquad \overset{|}{Cl}$	. . .

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARAC- TERISTICS.
	With Caustic Soda.	With Hy- drochloric Acid.	With Strong Acid.	On Dilution with Water.	
Black paste; violet solution in hot water.	Violet solu- tion with paste.	Cerise solu- tion with paste.	Blue.	Cerise.	Soluble in alco- hol.
Gray paste or bronze pow- der; insoluble.	Violet solu- tion with paste.	Cerise solu- tion with paste.	Blue.	Cerise.	Soluble in alco- hol.
Brown powder or paste; vio- let solution.	Brown ppt.	Cerise.	Blue.	Cerise.	Soluble in alco- hol.
Violet powder; violet solu- tion.	Brown ppt.	Blue.	Green.	Blue.	Soluble in alco- hol.
Brown powder; violet solu- tion.	Brown.	Violet ppt.	Bluish- green.	Violet ppt.	. . .
Bronze crystals; blue solution.	Red ppt.	Green crys- tals.	Yellow.	Blue.	Soluble in alco- hol.
Green powder; blue solution.	Red ppt.	Green crys- tals.	Orange.	Blue.	Soluble in alco- hol.
Violet powder; blue solution.	Brown ppt.	Violet.	Green.	Blue.	Soluble in alco- hol.
Green crystals; blue solution.	Blue ppt.	Red.	Green.	Red.	Soluble in alco- hol.
Brown powder; violet solu- tion.	. .	Redder.	Violet.	Blue ppt.	. . .
Black paste; blue solution.	Violet.	Red.	Red.	Claret.	Soluble in alco- hol.
Black paste or powder; blue solution.	. .	Blue ppt.	Red.	. .	Soluble in alco- hol.
Gray powder; blue solution.	Black ppt.	No change.	Brown.	Blue.	Soluble in alco- hol.
Black powder; violet - black solution.	Black ppt.	Black ppt.	Black.	Violet- black.	Soluble in alco- hol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Gallamine Blue.	(Base :) $(CH_3)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(3)OH \atop (4)OH \atop (6)CO.NH_2} \right.$ $\underset{OH}{\mid}$	From gallamic acid.
Celestine Blue B. Coreïne RR.	$(C_2H_5)_2N(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(3)OH \atop (4)OH \atop (6)CO.NH_2} \right.$ $\underset{Cl}{\mid}$	$\cdots$
Gallanilic Green. Fast Green G.	$(CH_3)_2(4)C_6H_3 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(4)O \atop (6)CO.NH.C_6H_5 \atop (3)NH.C_6H_5 \left\{ {SO_3NH_4 \atop NO_2} \right.} \right.$ (Probable.)	From tannin-anilide.
Fluorescent Blue. Resorcin Blue. Iris Blue.	$\left. {O(4) \atop Br(3) \atop Br(5)} \right\} C_6H \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_6H \left\{ {(4)O.NH_4 \atop (3)Br \atop (5)Br} \right.$	From resorufin.
Alizarin Green G.	$\left. {O(4) \atop HO(3)} \right\} C_{10}H_4 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_{10}H_5(6)SO_3H$	$\cdots$
Alizarin Green B.	$\left. {O(4) \atop HO(3)} \right\} C_{10}H_4 \left\{ {(2)O(2) \atop (1)N(1)} \right\} C_{10}H_5(4)SO_3H$	$\cdots$
Phenocyanine.	Uncertain.	Condensation of oxazines with resorcin.
Gallazin A.	Uncertain.	From gallocyanin.
Coreïne.	Uncertain.	From gallaminic acid.
Coreïne AR and AB.	Uncertain.	Action of aniline on coreïne.
Fast Green M.	Uncertain.	Action of aniline on muscarin.
Thiazines. Lauth's Violet.	$H_2N(4)C_6H_3 \left\{ {(2)S(2) \atop (1)N(1)} \right\} C_6H_3(4)NH_2.$ $\underset{Cl}{\mid}$	$\cdots$
Methylene Blue B.	$(CH_3)_2N(4)C_6Cl_3 \left\{ {(2)S(2) \atop (1)N(1)} \right\} C_6H_3(4)N(CH_3)_2$ $\underset{HCl}{\mid}$	$\cdots$
Thinonine Blue GO.	$(CH_3)_2N(4)C_6H_3 \left\{ {(2)S(2) \atop (1)N(1)} \right\} C_6H_3(4)N \left\{ {CH_3 \atop C_2H_5} \right.$ $\underset{Cl}{\mid}$	$\cdots$

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Gray paste; blue solution.	Violet.	Red.	Gray.	Red.	Chrome dye for wool.
Greenish-black powder; violet solution.	Violet.	Cerise.	Blue.	Cerise.	Soluble in alcohol.
Brown paste or powder; bluish-green solution.	Green ppt.	Blue ppt.	Carmine.	Brown ppt.	Chrome dye for wool.
Red paste filled with green crystals; violet solution with green fluorescence.	No change.	Brown ppt.	Blue.	Brown ppt.	. . .
Brown black powder; green solution.	Violet ppt.	Bordeaux ppt.	Bluish-green.	Red ppt.	Chrome dye for wool.
Greenish-black powder; green solution.	Green ppt.	Red ppt.	Violet.	Red ppt.	Chrome dye for wool.
Green paste; insoluble.	Brown solution becoming blue.	. . .	Brown solution becoming blue.	. .	Chrome dye for wool.
Brown paste; scarcely soluble.	Violet solution.	Red ppt.	Blue.	. .	Chrome dye for wool.
Green powder; blue solution.	Precipitate.	Red.	Blue.	Red.	Chrome dye for wool.
Blue paste; blue solution.	. .	Precipitate.	Violet.	Yellow.	Chrome dye for wool.
Brown powder; insoluble in water, soluble in acetic acid.	Red ppt.	Brown.	Violet.	Orange.	. . .
Greenish-black powder; violet solution.	Red ppt.	Bluer.	Green.	Violet.	Obsolete.
Dark blue or brown powder; blue solution.	Violet ppt.	No change.	Yellowish-green.	Blue.	Soluble in alcohol.
Brown powder; blue solution.	Violet ppt.	No change.	Yellowish-green.	Blue.	Soluble in alcohol.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Thiocarmine R.	$\left.\begin{array}{c}SO_3.C_6H_4.CH_2\\C_6H_5\end{array}\right\}$ $N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}$ $C_6H_3(4)N\left\{\begin{array}{c}C_2H_5\\CH_2.C_6H_4.SO_3Na\end{array}\right.$	. .
Toluidine Blue O.	$(CH_3)_2N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_6H_2\left\{\begin{array}{c}(4)NH.HCl\\(5)CH_3\end{array}\right.$	. .
New Methylene Blue N.	$\left.\begin{array}{c}C_2H_5NH(4)\\CH_3(3)\end{array}\right\}C_6H_2\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_6H_2\left\{\begin{array}{c}(3)CH_3\\(4)NH.C_2H_5\end{array}\right.$ $\underset{\mid}{} \; Cl$	. .
Brilliant Alizarin Blue G.	$(CH_3)_2N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_{10}H_3\left\{\begin{array}{c}(4)O\\(3)OH\\(7)SO_3Na\end{array}\right.$	. .
Brilliant Alizarin Blue R.	$HSO_3.C_6H_4.\!\!\begin{array}{c}C_2H_5\\CH_2\end{array}\!\!\Big\}\,N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_{10}H_4\left\{\begin{array}{c}(4)O\\(3)OH\end{array}\right.$	. .
Gentianin.	$(CH_3)_2N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_6H_3(4)NH.HCl$ $\underset{\mid}{} \; Cl$	. .
Methylene Green G.	$(CH_3)_2N(4)C_6H_3\left\{\begin{array}{c}(2)S(2)\\(1)N(1)\end{array}\right\}C_6H_2\left\{\begin{array}{c}(4)N(CH_3)_2\\(6)NO_2\end{array}\right.$ $\underset{\mid}{} \; Cl$	From methylene blue.

9. Quinoline and Acridine Dyestuffs.

This class of dyestuffs is not a very extensive one, and the precise constitution of many of its members is rather uncertain. Both quinoline and acridine, together with their homologues, are chromogenic bodies which give rise to dyestuffs by combining with a benzene residue and the subsequent introduction of amido-groups. Flavaniline and chrysaniline are typical representatives of this class. There also appears to be another class in which several quinoline groups are linked together by means of the methane residue, and hence they resemble somewhat in their constitution the diphenylmethane dyestuffs. The cyanines and quinoline yellow probably belong to this class, although the constitution of these bodies has not yet been satisfactorily explained.

Flavaniline. $C_{16}H_{14}N_2,HCl.$ When acetanilide is heated with zinc chloride to a temperature of 250°–270° C., it is converted into a coloring matter, the free base of which has the constitution of a para-amidophenyl-γ-lepidine, or γ-lepidine-ani-

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Blue powder; blue solution.	No change.	No change.	Yellowish-green.	Blue.	Soluble in alcohol.
Green powder; violet solution.	Violet ppt.	Blue.	Yellowish-green.	Blue.	Soluble in alcohol.
Metallic powder; blue solution.	Brown ppt.	No change.	Yellowish-green.	Blue.	Soluble in alcohol.
Brown paste; blue solution.	Violet.	Violet ppt.	Green.	Violet.	Soluble in alcohol.
Black paste; insoluble.	Blue ppt.	Green.	Green.	Violet.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	No change.	Yellowish-green.	Violet.	Soluble in alcohol.
Brown powder; green solution.	Violet ppt.	Greener.	Green.	Blue.	Soluble in alcohol.

l i n e.   The reaction consists in the conversion of acetanilide into the isomeric o r t h o - a m i d o - a c e t o - p h e n o n e, the subsequent conversion of a portion of this into *para*-amido-acetophenone, and the coalescence of one molecule of each of these bodies with elimination of water, thus:—

$$C_6H_5.NH.C(CH_3):O \quad = C_6H_4(NH_2).C(CH_3):O$$

Acetanilide.   *Amido-acetophenone.*

$$2C_6H_4(NH_2).C(CH_3):O = C_6H_4 \left\{ \begin{array}{l} C(CH_3):CH \\ N\!=\!=\!=\!\dot{C}(4)C_6H_4(1)NH_2 \end{array} \right. + 2H_2O$$

Amido-acetophenone.   *Para-amidophenyl-lepidins.*
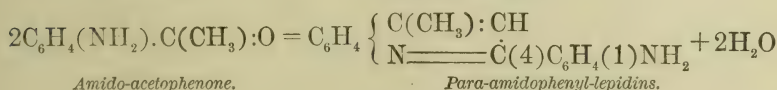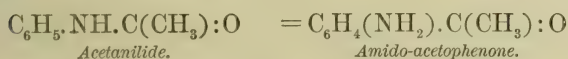
Flavaniline is now almost obsolete in commerce.   It is a hydrochloride of the base, and occurs as an orange-yellow crystalline powder, readily soluble in water with a yellow color.   The solution is unchanged by hydrochloric acid, but on adding soda yields a milky precipitate of the free base, soluble in ether, without color, but with a steel-blue fluorescence.   In strong sulphuric acid, flavan-

iline dissolves with a dirty-yellow color and blue fluorescence. Fla-
vaniline dyes wool and silk yellow without a mordant. Silk dyed
with flavaniline exhibits a fine moss-green fluorescence.

Flavaniline S is a sulphonated flavaniline. It resembles the
basic dye, but the solution is gradually decolorized by soda with-
out a precipitate being formed. In strong sulphuric acid it forms
a colorless solution, becoming yellow on dilution.

Quinoline Yellow. By heating quinaldin with phthalic anhy-
dride and chloride of zinc, a phthaleïn is formed of the composi-
tion:—

$$C_6H_4 : \left\{ \begin{matrix} CO \\ CO \end{matrix} \right\} : CH.C_9H_6N.$$
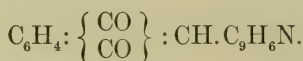
The product forms a yellow powder, which is insoluble in water,
but difficultly soluble in alcohol, to form a yellow solution. In
strong sulphuric acid the dye dissolves with a yellowish-red color,
the solution giving a flocculent yellow precipitate on dilution. By
sulphonation, quinoline yellow yields a d i s u l p h o n i c a c i d,
the sodium salt of which contains $C_6H_4 : (CO)_2 : CH.C_6H_4(SO_3Na)_2N$,
and is known as *water-soluble quinoline yellow.* It forms a bright
yellow powder, dissolving easily in water with an intense yellow
color, which is unaltered by dilute acids but is turned somewhat
darker by ammonia. The dye is not applicable to cotton. On
silk and wool, in a bath acidulated with sulphuric acid, it yields
very pure shades of yellow, which stand light fairly well.

Cyanine or QUINOLINE BLUE, $C_{29}H_{35}N_2I$, is obtained by heating
a mixture of quinoline and lepidine with an alkyl iodide in the
presence of an alkali. It is a strongly basic compound and its
mono-acid salts occur as beautiful blue crystals. It is not im-
portant as a dyestuff, as the shades obtained with it are very sensi-
tive to light and acids. It is insoluble in cold water, and only
slightly so in hot water, giving a violet-blue solution which smells
of quinoline. With strong sulphuric acid it evolves iodine on
heating. Of late this dyestuff has found application in the pre-
paration of isochromatic photographic plates.

QUINOLINE RED is a similar body obtained by the action of benzo-
trichloride on quinoline in the presence of zinc chloride. Its for-
mula is $C_{26}H_{19}N_2Cl$, and its constitution is probably analogous to
triphenylmethane:

$$C \left\{ \begin{matrix} C_6H_5 \\ CH_2.C_9H_6N \\ C_9H_6N.Cl \end{matrix} \right.$$
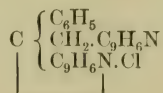
It occurs as small brownish-red needles, insoluble in cold water, though fairly soluble on warming. In alcohol it yields a red solution exhibiting an orange fluorescence. It is not employed to any extent as a dyestuff, but finds a similar use to cyanine, a mixture of the two constituting the so-called *Azalin*.

Aldehyde Green.[1] $C_{22}H_{27}N_3S_2O$. This coloring matter, now practically obsolete, is of interest as being one of the first green dyes obtained from aniline. It was prepared by the reaction of aldehyde on magenta and treatment of the product with sodium thiosulphate (hyposulphite). It formed an amorphous green powder, insoluble in water and but little soluble in alcohol, but readily soluble in a mixture of alcohol, water, and sulphuric acid.

Benzoflavine is the typical member of a series of basic dyestuffs obtained by the reaction of one molecule of benzaldehyde on meta-toluylene-diamine (or other aromatic meta-diamine) and one of its hydrochloride or sulphate. The product, $C_{21}H_{24}N_4,2HCl$, consisting of the hydrochloride of tetramido-ditolylphenylmethane, is heated with hydrochloric acid under pressure, when the hydrochloride of hydrodiamido-dimethyl-phenylacridine, $C_{21}H_{21}N_3$, is obtained, with elimination of ammonia. On exposure to air or treatment with an oxidizing agent of moderate power, such as ferric chloride, this body is oxidized to d i a m i d o - d i m e t h y l - p h e n y l a c r i d i n e or *benzoflavine*. The new coloring matter is a yellow substance soluble with difficulty in cold water, but more readily on heating. It is precipitated from its aqueous solution by dilute acids. In strong sulphuric acid it dissolves with yellow color and pronounced yellowish-green fluorescence. The alcoholic solution shows an intense yellowish fluorescence, which disappears on the addition of an acid. The free b a s e of benzoflavine is colorless and insoluble in water, but soluble in alcohol and ether. Benzoflavine is chiefly dyed on the cotton fibre, for which purpose the material is mordanted with tannin and tartar emetic. It yields a very pure yellow shade which is quite fast to soap and light. It is mostly used for shading malachite green and safranine, and in calico-printing.

ACRIDINE ORANGE, $C_{17}H_{19}N_3HCl + ZnCl_2$, is the zinc chloride double salt of tetramethyldiamido-acridine. It is a basic dyestuff resembling chrysaniline. Its solution in water and alcohol is orange in color and exhibits a green fluorescence. It gives orange

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[1] Also known as *Aniline Green* and *Usèbe's Green*.

shades on mordanted cotton which are very fast to soap. It is also used for dyeing leather, to which it imparts a peculiar golden lustre.

Chrysaniline. PHOSPHINE. This coloring matter, also called *Aniline Yellow, Aniline Orange,* and *Leather Yellow, Philadelphia Yellow G, Xanthin, Leather Brown, Phosphine II, N,* and *P, Patent Phosphine* and *Nankin,* is obtained as a secondary product of the manufacture of magenta.[1]

Pure chrysaniline has the constitution of a d i a m i d o-
p h e n y l - a c r i d i n e :—

$$C_6H_4 : \left\{ \begin{matrix} N \\ \dot{C} \end{matrix} \right\} : C_6H_3 . NH_2 \; ; \; \text{ or } \; N \left\{ \begin{matrix} C_6H_4 . NH_2 \\ C_{13}H_7 . NH_2 \end{matrix} \right.$$
$$\overset{|}{C_6H_4} . NH_2$$
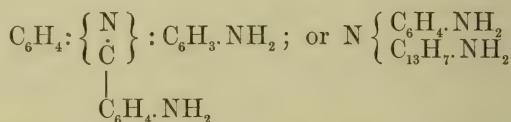
The commercial product *phosphine* is usually the n i t r a t e or according to B e n e d i k t the h y d r o c h l o r i d e, of chrysaniline, mixed with more or less of the corresponding salt of the homologue c h r y s o t o l u i d i n e, $C_{20}H_{17}N_3$.

Commercial *phosphine* forms an orange-yellow powder, readily soluble if the hydrochloride, but difficultly if the nitrate, to a reddish-yellow solution. It is also soluble in alcohol. Dilute hydrochloric acid simply deepens the color, but with excess of the strong acid a d i h y d r o c h l o r i d e is precipitated, readily soluble in pure water. Ammonia and soda liberate free c h r y s a n i l i n e as an amorphous yellow precipitate, which melts on boiling, the liquid being colored pale yellow. The precipitate is soluble in ether. Phosphine dissolves in strong sulphuric acid to form a reddish-yellow solution which exhibits a strong green fluorescence. On dilution, a reddish-yellow solution is obtained.

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[1] The resinous bye-products contain chrysaniline, mauvaniline, violaniline, a little rosaniline, and undefined resinous matters. On boiling the mass with dilute hydrochloric acid, resins and violaniline remain insoluble. By fractional precipitation of the filtered solution with lime, mauvaniline, rosaniline, and chrysaniline are successively precipitated. Chrysaniline may be more easily prepared from the mother-liquors which remain after precipitating the magenta by salt, in the arsenic acid process. More salt is added to the liquid and then lime, the precipitate treated with dilute nitric acid, and the sparingly soluble nitrate of chrysaniline precipitated by adding excess of nitric acid to the solution. The deliberate synthesis of chrysaniline has been effected by heating benzoic acid and diphenylamine with zinc chloride, nitrating the resultant phenylacridine, and reducing it to the diamido-derivative.

On adding nitric acid or sodium nitrate to a tolerably concentrated solution of phosphine, the sparingly soluble c h r y s a n i -l i n e n i t r a t e separates as a red crystalline precipitate.   In warm solutions, the precipitate is produced slowly, and on stirring the liquid is deposited in streaks in the track of the glass rod.   Under the microscope the precipitate is seen to consist of needles.   This characteristic reaction, when carefully applied, distinguishes phosphine from other yellow coloring matters, but is liable to fail in solutions of the nitrate.   Hence a preferable plan is to liberate the base by ammonia, agitate with ether, treat the separated ethereal solution with dilute acetic acid, concentrate the acetic solution, and add sodium nitrate.   This mode of operating excludes the possibility of confusion with n i t r o - c o m p o u n d s , which often yield yellow crystalline precipitates on treating their solutions with nitric acid or potassium nitrate.   But the nitro-dyes are not extracted by agitating their ammoniacal solutions with ether, though, unlike chrysaniline, most of them are extracted from their acidulated solutions.   Nitro-compounds are further distinguished by the red or brownish color developed on boiling with potassium cyanide; whereas phosphine gives a yellow precipitate in the cold, and the liquid acquires a yellow color on boiling.

On treatment with stannous chloride and hydrochloric acid, chrysaniline solutions are decolorized, but the yellow color rapidly returns on exposing the reduced liquid to the air.

When heated with 3 or 4 parts of hydrochloric acid to 160°–180° C., chrysaniline is decomposed with formation of ammonium chloride and c h r y s o p h e n o l , $C_{19}H_{15}N_2O$, in the same way that flavaniline yields flavenol, and auramine tetramethyl-benzophenone.

Phosphine behaves to fibres like the other basic aniline dyes. It produces a yellow on silk or wool, and is used in admixture with magenta for dyeing silk scarlet.   On cotton mordanted with aluminium acetate it gives a nankin-yellow which will stand soaping.

Acids redden fibres dyed with phosphine, and after a time the coloring matter is removed.   Alkalies turn the fibre to a greenish-yellow paler than the original.   Reducing agents decolorize it gradually.

COMMERCIAL NAME.	FORMULA.	REMARKS.
Quinolines. Flavaniline.	$C_6H_4 \begin{cases} (1)C \begin{cases} CH_3 \\ CH \end{cases} \\ (2)N = C(4)C_6H_4(1)NH_2.HCl \end{cases}$	From acetaniline.
Flavaniline S.	Sodium salt of flavaniline sulphonic acid.	From flavaniline.
Quinoline yellow (spirit soluble).	$C_6H_4 \begin{cases} (1)CO \\ \quad > O \\ (2)C = CH.C_9H_6N \end{cases}$	From quinaldine.
Quinoline yellow (water soluble).	Sodium disulphonate of the preceding.	From the above dyestuff.
Cyanine.	Uncertain.	From amyl iodide.
Quinoline Red.	$C \begin{cases} C_6H_5 \\ CH_2.C_9H_6N \\ C_9H_6N.Cl \end{cases}$	From quinaldine and isoquinoline.
Aldehyde Green.	Quinoline derivative of rosaniline.	From aldehyde and rosaniline.
Acridines. Benzoflavine.	$\begin{matrix} NH_2(4) \\ CH_3(5) \end{matrix} \Big\} C_6H_2 \begin{cases} (2)N(2) \\ (1)C(1) \end{cases} C_6H_2 \begin{cases} (4)NH_2.HCl \\ (5)CH_3 \end{cases} \\ \qquad\qquad C_6H_5$	· · ·
Acridine Orange.	$(CH_3)_2N(4)C_6H_3 \begin{cases} (2)N \ (2) \\ (1)CH(1) \end{cases} C_6H_3(4)N(CH_3)_2.HCl \\ \qquad\qquad\qquad + ZnCl_2$	· · ·
Acridine Orange R.	$(CH_3)_2N(4)C_6H_3 \begin{cases} (2)N(2) \\ (1)C(1) \end{cases} C_6H_3(4)N(CH_3)_2.HCl \\ \qquad\qquad C_6H_5$	· · ·
Acridine Yellow.	$\begin{matrix} NH_2(4) \\ CH_3(5) \end{matrix} \Big\} C_6H_2 \begin{cases} (2)N \ (2) \\ (1)CH(1) \end{cases} C_6H_2 \begin{cases} (4)NH_2.HCl \\ (5)CH_3 \end{cases}$	· · ·
Chrysaniline. Phosphine.	$C_6H_4 \begin{cases} (2)N(2) \\ (1)C(1) \end{cases} C_6H_3(4)NH_2 \\ \quad C_6H_4(4)NH_2$	From magenta residues.

CHARACTER OF DYESTUFF.	REACTION OF AQUEOUS SOLUTION.		REACTION OF DYE WITH SULPHURIC ACID.		OTHER CHARACTERISTICS.
	With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.	
Orange crystals; yellow solution.	White ppt.	No change.	Colorless.	. .	Obsolete.
Orange powder; yellow solution.	Decolorized.	No change.	Colorless.	Yellow.	Obsolete.
Yellow powder; insoluble.	. .	. .	Orange.	Yellow ppt.	Soluble in alcohol. Dye for varnishes.
Yellow powder; yellow solution.	Darker.	Brighter.	Orange.	Yellow.	Soluble in alcohol.
Green crystals; blue solution.	Blue ppt.	Colorless.	Colorless.	Colorless.	Used in photography.
Red crystals; red solution.	. .	. .	Colorless.	Red.	Soluble in alcohol. Used in photography.
Green powder; insoluble.	. .	. .	. .	. .	Soluble in alcohol.
Orange powder; yellow solution.	Pale yellow ppt.	Orange ppt.	Greenish-yellow.	Orange ppt.	Soluble in alcohol.
Orange powder; orange solution, green fluorescence.	Yellow ppt.	Red.	Colorless.	Orange.	Soluble in alcohol.
Orange powder; orange solution, with green fluorescence.	Yellow ppt.	Red.	Colorless.	Orange.	Soluble in alcohol.
Yellow powder; yellow solution, green fluorescence.	Yellow ppt.	Yellow ppt.	Yellow.	Yellow ppt.	Soluble in alcohol.
Orange powder; orange solution.	Yellow ppt.	Brighter.	Orange.	Orange.	Soluble in alcohol.

10. Thiobenzenyl or Thiazol Dyestuffs.

There is a small, yet important, group of coloring matters, including primuline and the thioflavines, in which the chromophoric group appears to consist of a five-membered ring built up of sulphur, nitrogen and carbon. The constitution of this ring seems to conform to the following scheme:

$$\begin{matrix} -C-S \\ | \quad\quad \diagdown \\ -C-N \diagup \end{matrix} C-$$
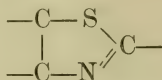
The two carbon atoms on the one side being in a benzene nucleus, while the other carbon atom is a methane residue. Dehydrothioparatoluidine may be considered as the starting point in the preparation of the thiazol dyes. This substance is an amidobenzenyl-toluylmercaptan and has the following constitution:

$$CH_3 \overset{-S}{\underset{-N}{\bigcirc}} \diagdown C \diagdown \diagup \quad NH_2 \text{ or}$$

$$CH_3(4)C_6H_3 \left\{ \begin{matrix} (2)S \\ (1)N \end{matrix} \right\} C(1)C_6H_4(4)NH_2.$$
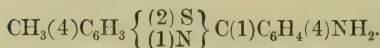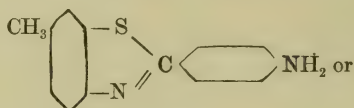
The general method of preparation of the thiazol dyestuffs is the action of sulphur on paratoluidine or its homologues. By heating a mixture of these two substances dehydrothio-paratoluidine is obtained; if the reaction is continued for a longer period of time, another product is obtained which is distinguished from the former by its intense color and slight solubility and basicity. This substance is primuline, and appears to contain three thiazol rings:—

$$CH_3.C_6H_3 \left\{ \begin{matrix} S \\ N \end{matrix} \right\} C\, C_6H_3 \left\{ \begin{matrix} S \\ N \end{matrix} \right\} C\, C_6H_3 \left\{ \begin{matrix} S \\ N \end{matrix} \right\} C.C_6H_3 \left\{ \begin{matrix} SO_3Na \\ NH_2 \end{matrix} \right.$$
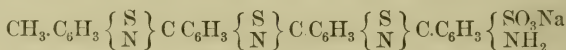
The thiazol dyestuffs are all yellow, and readily soluble in water.

Thioflavine T, $C_{17}H_{19}N_2SCl$, is the trimethyl chloride derivative of dehydro-thiotoluidine, and has the following constitution:—

$$CH_3(4)C_6H_3 \left\{ \begin{matrix} (2)S \\ (1)N \end{matrix} \right\} C.(1)C_6H_4(4)N(CH_3)_3Cl.$$

It is obtained by the action of methyl chloride on dehydrothiotoluidine or by the action of methyl alcohol and hydrochloric acid. It is brought into commerce in the form of a yellow crystalline powder which is easily soluble in water and alcohol with a yellow color, the solutions possessing a green fluorescence, especially the

alcoholic solution. The aqueous solution is unaffected by the addition of caustic soda or hydrochloric acid. With strong sulphuric acid the dyestuff gives a colorless solution which becomes yellow on dilution with water. Thioflavine T is used for dyeing silk and cotton mordanted with tannin; the shades so obtained are a fine greenish-yellow, which on silk exhibit a green fluorescence.

Thioflavine S is a dyestuff produced in the same reaction with the above, being separated from the former by means of its sparing solubility in dilute hydrochloric acid. The dyestuff is a sulphonic acid salt which is sold in the form of a yellow powder, soluble in water and alcohol with a yellow color, the solution in the latter possessing a green fluorescence. The addition of caustic soda causes no change in the aqueous solution, but hydrochloric acid throws down an orange-yellow precipitate. The dyestuff dissolves in strong sulphuric acid to a brownish-yellow solution, from which an orange precipitate separates on dilution with water. Thioflavine S dyes unmordanted cotton from an alkaline bath, but the shades produced are not fast to light or acids, though they resist alkalies fairly well. They are unaffected by reducing agents and cannot be stripped from the fibre.

Primuline,[1] $C_{28}H_{17}N_4O_3S_4Na$, of which the composition has been given on page 368,[2] is obtained by heating two molecules of para-toluidine with four to five equivalents of sulphur at 200° to 280° C.; the primuline base so obtained is then treated with fuming sulphuric acid. The commercial product is a yellow powder, which is very soluble in hot water. The very dilute aqueous solution of primuline exhibits a blue fluorescence. In a 5 per cent. neutral

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[1] Also known as *Carnotin, Polychromine, Thiochromogene, Aureolin,* and *Sulphine.*

[2] G r e e n represents the constitution of the primuline base by the formula:

$$CH_3.C_6H_3\left\{\begin{matrix}-N{=}CH-\\-S-\end{matrix}\right\}\ C_6H_2\left\{\begin{matrix}-N{=}CH-\\-S-\end{matrix}\right\}\ C_6H_2\left\{\begin{matrix}-N{=}CH-\\-S-\end{matrix}\right\}C_6H_3.NH_2$$
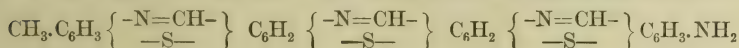
but P f i t z i n g e r and G a t t e r m a n n (Ber. xxii, 1063) contend that the formula should be:

$$CH_3.C_6H_3\left\{\begin{matrix}-N{=}\\-S-\end{matrix}\right\}\ C.\dot{C_6}H_3\left\{\begin{matrix}-N{=}\\-S-\end{matrix}\right\}\ C.C_6H_3\left\{\begin{matrix}-N{=}\\-S-\end{matrix}\right\}C.C_6H_4.NH_2.$$
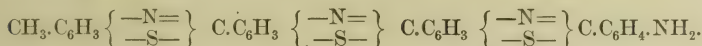
since his reactions appear to indicate that the formula for dehydrothiotoluidine should be:

$$CH_3.C_6H_3\left\{\begin{matrix}-N{=}\\-S-\end{matrix}\right\}C.C_6H_4.NH_2,$$
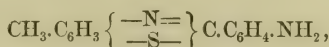
and not $CH_3.C_6H_3\left\{\begin{matrix}-N{=}CH-\\-S-\end{matrix}\right\}C_6H_3.NH_2$ as given by Green.

bath at a boiling temperature, primuline dyes cotton a lemon-yellow color, which is tolerably fast to scouring, entirely unaffected by alkalies, and turned a golden yellow by acids. The affinity of the fibre for the coloring matter is increased, and consequently deeper shades may be obtained, by addition of sodium chloride or sulphate to the bath. Reducing agents produce no change, but the color is attacked by oxidizing agents, such as bleaching powder or chromic acid. By the latter the shade is changed to olive, while boiling solutions of hypochlorites turn the color to orange-yellow, which is very fast to all agents.

The aqueous solution of the dyestuff is unaffected by the addition of caustic soda, while hydrochloric acid throws down a yellow precipitate. The dyestuff dissolves in strong sulphuric acid to a pale yellow solution with a green fluorescence; dilution with water causes the separation of an orange-yellow precipitate.

Since primuline contains an amido-group, it is capable of being diazotized, and this operation may be readily performed on the dyed fibre by passing the washed material through a dilute solution of sodium nitrite (3 to 5 per cent.) acidulated with sulphuric acid. If the fabric be then again washed and immersed without delay in a developing solution of one of the naphthols, naphthylamines, or their derivatives, various shades of yellow, orange, scarlet, or maroon may be obtained.[1] The colors so obtained are termed *ingrain colors*, and are characterized by their extraordinary fastness to scouring, milling, acids, etc., being said to be only equaled in this respect by alizarin and its congeners, and to far exceed the ordinary benzidine dyes.

CHLORAMINE YELLOW is a dyestuff of unknown constitution, obtained by the oxidation of dehydrothiotoluidine-sulphonic acid. It is a brownish-yellow powder, soluble in water with a yellow color, but insoluble in alcohol. The addition of either hydrochloric acid or sodium hydrate to the solution produces an orange-yellow precipitate. With strong sulphuric acid the dyestuff yields

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[1] The following shades are obtained with the different developers:

    With beta-naphthol, red.
    With beta-naphthol-disulphonic acid R, maroon.
    With resorcinol, orange.
    With phenol, yellow.
    With meta-phenylene-diamine, brown.
    With alpha-naphthol-sulphonic acid NW, crimson.
    With benzyl-naphthylamine and ethyl-betanaphthylamine, bordeaux.

a deep red solution from which a light brown precipitate is thrown out on dilution with water. Chloramine yellow produces pure yellow shades on wool and unmordanted cotton, which are fast to light.

OXYPHENINE, OXYPHENINE GOLD, CHLOROPHENINE G and THIO-PHOSPHINE J are dyestuffs which are produced in a manner similar to the above, and no doubt possess an analogous constitution. Their properties and application are the same as chloramine yellow.

CHROMINE G is a dyestuff similar to thioflavine S, and is obtained by the action of sulphur at elevated temperatures on dehydrothiotoluidine, methylating the product so obtained, and then sulphonating by means of fuming sulphuric acid. It is a yellowish-brown powder, giving a yellow solution in water and alcohol. The aqueous solution treated with hydrochloric acid suffers scarcely any change, a slight brownish precipitate being formed. Caustic soda turns the solution to a greenish-yellow. Strong sulphuric acid dissolves the dyestuff to a greenish-yellow solution, exhibiting a blue fluorescence and giving an orange precipitate on dilution with water. Chromine G is employed in the same manner as Thioflavine S, yielding fine yellow shades which are fast to soap but very fugitive to light.

MIMOSA is a diazotized compound of primuline, treated with ammonia. Its formula and constitution has not been determined. It is sold in the form of a yellowish-brown powder, soluble in water and alcohol with a yellow color. With hydrochloric acid the aqueous solution throws down an orange precipitate, while sodium hydrate gives a scarlet precipitate. Strong sulphuric acid gives a yellowish-brown solution, which on dilution with water yields a brown precipitate and evolves nitrogen. Mimosa dyes a yellow on unmordanted cotton which is fast to soap but fugitive to light.

11. Dyestuffs of Unknown Constitution.

There are a few dyestuffs having a technical importance whose chemical constitution is either very uncertain or totally unknown. Such, for instance, are aniline black, cachou de laval, thiocatechine, the ursol blacks, vidal black, and the direct greys.

Aniline Black. By the oxidation of aniline under suitable conditions a very stable black coloring-matter is formed. The most perfect black is yielded by pure aniline boiling at 182° C.

Orthotoluidine gives a bluish-black and paratoluidine a brown-black.[1]

The oxidation of aniline to aniline black may be effected by potassium bichromate, permanganate, or chlorate, and by various other oxidizing agents.[2] In practice, a readily changeable metallic salt is employed as a carrier of oxygen, a very suitable combination being a chlorate (preferably that of sodium) and cupric sulphate. Ammonium vanadate now receives an application in the production of aniline black, as it is readily reduced to vanadium chloride, and this is immediately reoxidized to a vanadate by the chlorate simultaneously employed. One part of vanadium will do the duty of 4000 of copper, and suffice for the production of from 10,000 to 20,000 parts of aniline black. Electrolytic oxygen may also be employed for producing aniline black.

To produce aniline black in a pure state, 40 parts of aniline hydrochloride, 40 of cupric sulphate, 20 of potassium chlorate, and 16 parts of ammonium chloride should be dissolved in 500 parts of water, and the solution heated to about 60° C. The black precipitate formed may be purified, if desired, by boiling it successively with hydrochloric acid, alcohol, ether, benzene, and chloroform. The product is the hydrochloride of a base called n i g r a n i l i n e, which may be obtained in a free state by treating the coloring matter with a dilute alkali.

Nigraniline has the empirical formula C_6H_5N, and consequently possesses the same percentage composition as a z o b e n z e n e. Its molecular formula, according to N i e t z k i, is probably $C_{30}H_{25}N_5$. According to L i e c h t i and S u i d a, however, aniline black is a chlorinated base called e m e r a l d i n e, containing $C_{18}H_{14}ClN_3$, all the salts of which contain chlorine, which cannot be removed even by treatment with argentic oxide. Nigraniline is a weak base, and combines with two equivalents of acids to form a series of dark green salts, which are insoluble in and partially decomposed by water.

Aniline black is turned dark green by sulphurous acid, and other

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[1] NAPHTHAMEÏN, or Naphthalene Violet, is a coloring matter produced by treating the hydrochloride of alphanaphthylamine with ferric chloride or other oxidizing agent. It forms an amorphous, purple precipitate, insoluble in water, alkalies, and dilute acids, and only sparingly soluble in alcohol, but readily soluble in ether or acetic acid. In strong sulphuric acid it dissolves with blue color.

[2] F l i n t o ff has shown that magenta is sometimes formed during the development of aniline black on cotton.

mineral acids also affect it; but if it be treated with an acid solution of potassium bichromate the black color becomes permanent, and is no longer affected by treatment with acids or reducing agents. According to Liechti and Suida, this unalterable black is not a chromate of the base, but the compound of an oxidation-product with chromic oxide (Cr_2O_3).

By treatment with tin and hydrochloric acid, aniline black is reduced to p a r a d i a m i d o b e n z e n e, p a r a d i a m i d o - d i p h e n y l a m i n e, and other products.

Powerful oxidizing agents, such as chromic acid mixture, convert aniline black into q u i n o n e, $C_6H_4O_2$.

Aniline black dissolves in strong sulphuric acid to form s u l - p h o n i c a c i d s, which are insoluble in acidulated water, and are, therefore, precipitated on adding water to the solution. On protracted washing with water the precipitate dissolves with green color. The alkali-metal compounds of sulphonated aniline black dissolve in water with blue-black color. The solutions are decolorized by reducing agents (e. g., zinc-powder, glucose), but recover their original tint on exposure to air. The fact is employed for the preparation of an aniline-black vat.

On heating aniline black with aniline acetate, an i n d u l i n e is formed, the hydrochloride of which crystallizes in needles having a coppery lustre.

Aniline black differs remarkably from most other aniline colors in that it is wholly insoluble in water, alcohol, acids, soap-lye, and alkaline solutions. Hence the application of ready-formed aniline black is very limited, and it is usually produced in the fibre itself. It yields an extremely fast and pure black on cotton, but it is not well suited for dyeing silk or wool. Its chief application is in the dyeing of cotton hosiery where its great fastness and permanence render it an especially desirable dye. Many precautions, however, must be employed in the proper dyeing of it, as it is a process which is very liable to tender the fibre, owing to the acid fumes liberated in the oxidation of the dyestuff.

On the fibre, aniline-black is easily recognized by its resistance to reagents,[1] being unchanged by alkalies, and either wholly unchanged by acids or turned slightly greenish, the black color being

[1] Fibres dyed with *logwood black* leave on ignition an ash containing iron or chromium, as also do *madder* and *tannin blacks*. These blacks are reddened by dilute hydrochloric acid, and are readily bleached by bromine water or hypochlorites.

restored by alkalies. Weak oxidizing agents have no effect, but if the fibre be treated alternately with strong solutions of potassium permanganate and oxalic acid, several times in succession, the color will be destroyed. Hypochlorites change the color to brownish-red, but if the fibre thus treated be washed and exposed to the air it slowly becomes black again.

Canarin. $C_3S_3N_3H$. This coloring matter, sometimes called *persulphocyanogen yellow*, is not strictly a coal-tar dye, as it is produced by the action of an oxidizing agent, such as chlorine or nitric acid, on a thiocyanate (sulphocyanide). It will be considered at greater length in another volume in the chapter on "Cyanogen Compounds." Canarin forms an orange-yellow powder insoluble in water, alcohol, or ether. It dissolves in alkalies with yellow color, and on addition of hydrochloric acid is reprecipitated from the solution in orange- yellow flocks. It dissolves in strong sulphuric acid, but is reprecipitated on adding water. It has been employed in calico-printing, but at present it is obsolete as a dyestuff.

MUREXIDE, $C_8H_4N_5O_6.NH_4$, is the ammonium salt of purpuric acid, and is a uric acid derivative. It occurs in the form of brown crystals, having a greenish lustre. It gives a red solution with water, which is decolorized by the addition of hydrochloric acid. Caustic soda causes the solution to become bluer. With strong sulphuric acid murexide gives a yellow solution, which is decolorized by dilution with water. As a dyestuff murexide is no longer commercially employed; formerly it was to be met with under the name of Rouge de Naples.

URSOL D and P are oxidation products of paraphenylenediamine, and may possess the formula:

$$C_6H_4 \left\{ \begin{array}{c} (1) \overset{/OH}{\underline{\quad}} NH(1) \\ (4) \underset{\backslash OH}{\underline{\quad}} NH(4) \end{array} \right\} C_6H_4$$
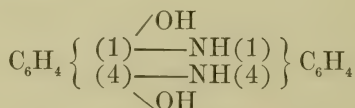
These colors are produced on the fibre by oxidation; they yield brown to black shades, and are used chiefly for dyeing furs.

THIOCATECHINE is a sulphuretted dyestuff, obtained by heating paradiamines or acetyl-nitramines with a mixture of sulphur and sodium sulphide. It is soluble in alkalies and alkaline sulphides; with strong sulphuric acid it gives a brownish-red solution, which is precipitated by the addition of water. It gives a fast catechu-

brown shade on cotton.   *Thiocatechine S* is thiocatechine which has been purified and dissolved in an alkaline sulphide.

CACHOU DE LAVAL is a dyestuff of peculiar composition produced by melting various organic substances, such as sawdust, bran, leaves, etc., with alkaline sulphides.   It is soluble in water, but is precipitated on prolonged boiling.   It appears to behave like a reduced coloring matter which is developed by means of oxidation. It yields brown and grayish-brown colors on cotton, which serve as a bottom shade and mordant for other adjective dyestuffs.   The shades obtained are quite fast to light and exceedingly fast to soap. On the addition of acids to the dyestuff hydrogen sulphide is liberated, and the coloring matter together with sulphur is precipitated.   *Cachou de Laval S* is the dyestuff purified from excess of alkaline sulphide.   It is used in calico-printing.

NOIR DE LYON is a black dyestuff obtained by the action of sodium and bichromate of potash on resorcin.   It dyes a blue-black on silk and wool.

VIDAL BLACK is a dyestuff produced by heating a mixture of sodium sulphide and sulphur with para-amidophenol or paraphenylenediamine.   It is sold in the form of black porous lumps, smelling of hydrogen sulphide.   It gives a dark green solution with water, which is precipitated by the addition of hydrochloric acid with the simultaneous evolution of hydrogen sulphide.   Caustic soda gives a green precipitate.   The dyestuff is insoluble in strong sulphuric acid, and on diluting with water hydrogen sulphide is evolved.   Vidal black is dyed on unmordanted cotton from an alkaline bath, and subsequently oxidized by means of bichromate of potash.   The shades vary from a bluish-green to a bluish-black, depending upon the amount of dyestuffs employed. The blacks obtained are very fast to soap, light, acids and alkalies, but are liable to crock.   The fibre is also apt to be much tendered after dyeing with vidal black.

ST. DENIS BLACK V is a substance similar to the above, being in fact an improvement in the manufacture of the latter.   It is similar in its properties to vidal black, but does not possess the disadvantages of the latter, and is more readily applied to the fibre.

ITALIAN GREEN is another sulphuretted dyestuff obtained by heating para-nitrophenol with a mixture consisting of sulphur, caustic soda and copper sulphate to 180–200° C.   It occurs in the form of black porous lumps, dissolving in water to a green solution, which is precipitated on exposure to the air.   On treatment with

acids the aqueous solution gives a black precipitate, sulphur separates out, and hydrogen sulphide is evolved. It dyes cotton a green color from a neutral bath.

URANIA BLUE is an oxidation product of a mixture of beta-dinaphthyl-metaphenylenediamine-disulphonic acid with para-amido-dimethylanilinethiosulphonic acid. It is a blue-violet powder, soluble in water with a blue color; the solution is unaffected by either hydrochloric acid or caustic soda. With strong sulphuric acid it gives a green solution, becoming blue on dilution with water. It gives blue shades on wool and silk in an acid bath.

DIRECT GRAY J, (B, R, and 4 R[1]) is prepared by boiling nitro-sodimethyl-aniline hydrochloride with water or alcohol.

It is sold in the form of a black powder which dissolves in water and alcohol with a reddish-gray color. Hydrochloric acid causes the solution to become blue, and caustic soda gives a black precipitate. Strong sulphuric acid dissolves the dyestuff to a green solution which becomes reddish-gray on dilution with water. It gives fine silver-gray shades on either mordanted or unmordanted cotton.

CHROMOGEN I is the sodium salt of chromotropic acid. It is a cream-colored powder soluble in water and alcohol, giving colorless solutions which are unaffected by either hydrochloric acid or caustic soda. The dyestuff itself is developed on the fibre by oxidation with bichromate of potash, when brown shades are produced which are very fast to light, soap, acids, and alkalies.

12. Coloring Matters of Natural Origin.

The dyes occurring naturally in animal or vegetable products, or which can be produced therefrom by comparatively simple means, are very numerous and interesting; and there is no doubt that the methods for their extraction or production would have been greatly improved of late years had not the coal-tar dyes engrossed the attention of nearly all investigators actively interested in the chemistry of coloring matters. The use of some of the natural coloring matters has greatly decreased, owing to the rivalry of the coal-tar dyes, and the production of some of them is nearly, if not wholly, a thing of the past. Thus the azo-scarlets have greatly diminished the consumption of cochineal, while artificial alizarin has nearly extinguished the natural dye from madder; and alizarin-blue and

[1] Also known as *New Gray, Methylene Gray O, ND*, and *NF; New Methylene Gray G* and *B; Nigrisine, Malta Gray*, and *Alsace Gray*.

the indulines now compete with indigo, which is itself producible by complex synthetical processes from the coal-tar constituent t o l u e n e, C_7H_8. In fact, even the natural production of indigo itself is being seriously threatened at present by the artificial production of this coloring matter from coal-tar products.

The dyes and coloring matters of natural origin may be conveniently classified under the following heads:—

INDIGO, and allied coloring matters.

LICHEN DYES, such as orchil, cudbear, litmus.

RED DYES FROM WOODS, &c., as Brazil-wood and logwood.

YELLOW VEGETABLE DYES, such as saffron, turmeric, weld.

CHLOROPHYLL and its allies; and

ANIMAL DYES, such as cochineal.

Of the coloring matters included in the above arrangement, *madder* has already been referred to under the heads of a l i z a r i n and p u r p u r i n; *chlorophyll* and many other plant-colors receive little or no practical application, and hence need not be specially described; while the coloring matters of blood, bile, urine, etc., will be better considered in the sequel.

Indigo.

Indigo is the product of various species of leguminous plants of the genus *Indigofera*,[1] which appear to be indigenous in Cambay, but are also cultivated in India, China, Java, and other parts of the East. It is also grown in the West Indies and South America, and the species *Indigofera argentea* is cultivated in Egypt and Arabia.

Indigo does not exist ready-formed in the above plants, but is produced by the decomposition of a glucoside called i n d i c a n, $C_{26}H_{31}NO_{17}$, which may be extracted from them by cold alcohol.

To obtain indigo from the plants, the chopped leaves or twigs are completely covered with water. Fermentation sets in, and continues from nine to fourteen hours, according to the temperature. When complete, the water is run off into shallow vats, where

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[1] The most valued and extensively cultivated species is the *Indigofera tinctoria*, but *I. disperma*, *anil*, and *argentea* are also widely grown. Less important species are *I. hirsuta*, *pseudo-tinctoria*, *sericea*, *cytisoides*, *angustifolia*, *triplia*, *glabra*, *glauca*, &c. *Indigofera tinctoria* is grown from seeds, and is a herbaceous plant with a single stalk, growing to a height of 3 feet or a little more, and about the size of the finger. The value of the crop is almost in proportion to the abundance of leaves, as the coloring matter exists chiefly in that part of the plant.

it is subjected to agitation to expose it to the air.[1] The yellow liquid thereby assumes a greenish color, and the indigo separates in flakes. After standing for an hour, the blue pulpy indigo is separated, and boiled with water to prevent secondary fermentation and the consequent formation of objectionable brown products.[2] After standing twenty-four hours, the liquid is again boiled, and then passed through a coarse filter. The precipitate is separated, pressed, and dried slowly in sheds, from which the light is carefully excluded.[3]

The indigo thus obtained varies greatly in quality, both in respect to the proportion of blue coloring matter it contains and in its freedom from objectionable impurities.

Indigo may also be obtained from several plants besides the *Indigofera*, but these are more generally used directly for dyeing blue than for extracting the indigo. The most important of these indigo-yielding plants are *Isatis tinctoria* or w o a d, once extensively cultivated both in England and on the Continent; *Polygonum tinctorium* and *Nerium tinctorium; Asclepias tingens; Eupatorium tinctorium*, one of the Compositæ; and several species of o r c h i d s, which, when cut, become blue at the section after exposure to the air.

Woad or *pastel* is a biennial cruciferous plant. The leaves, of which two crops are yielded, are gathered in the second year, and are rapidly washed and dried. They are used directly for dyeing, or are made into a paste with water, piled in heaps, allowed to fer-

[1] Some manufacturers add a little lime-water at this stage, while J. S a y e r s recommends the addition of ammonia during the fermentation. By this means the yield of coloring matter may be increased fully 100 per cent. (*Jour. Soc. Dyers, &c.*, ii. 141).

[2] C. J. von Lookeren (*Chem. Zeit.*, xxiii. 165) gives the following theory for the formation of indigo : In the usual so-called fermentation of indigofera leaves, water is absorbed and the indican partially broken up in the course of its diffusion to the outer part of the leaf by means of an enzyme in the (dead) protoplasm, being covered with indigo white, other nitrogenous substances, and glucose. The indigo white, undecomposed indican, and other substances, dissolve in the surrounding liquid, producing a faintly alkaline solution (to litmus as indicator). On oxidation the indigo white is converted into indigo blue, and indigo brown, which is formed from another product, separating with it, whilst the other products are left in solution. Indigo red (indirubin and resinous substances) may consist in part of an oxidation product of indican decomposed by the oxygen absorbed or otherwise.

[3] The best qualities of indigo are usually those manufactured by Europeans, who operate with more care than the natives.

ment for fourteen days, and then made into small balls and dried. The product is sometimes again moistened with water and subjected to a second fermentation, during which ammonia is evolved. The best woad comes from France. The balls are light, of a green or yellowish-green color, and have a sickly odor. When cut, woad should exhibit a soft, shining surface, and when rubbed on paper should leave a green mark. It improves by keeping, and some manufacturers consider that the finest shades of indigo-dyeing cannot be obtained without an admixture of woad.

Isatis indigotica is cultivated in some parts of China for the preparation of a variety of indigo which is sold in the form of paste. When dried it appears blackish, and is used in producing *Canton blue*, &c.

Polygonum tinctorium is also indigenous to China, and yields an indigo of superior quality. It is also used for dyeing directly. The attempts made to acclimatize the plant in Europe have been unsuccessful.

A substance allied to indican sometimes occurs in urine, and gives rise, by its conversion into indigo-blue, to a blue coloration of the liquid when left in contact with the air, or when treated with sulphuric acid.[1]

Indican, $C_{26}H_{31}NO_{17}$, already referred to as the natural glucoside by the decomposition of which indigo-blue is produced, was first isolated by E. S c h u n c k.[2] It forms a transparent brown syrup, from which it is impossible to separate the water without causing decomposition. The aqueous solution has a yellow color, bitter taste, and slight acid reaction. When boiled with caustic alkali it evolves ammonia. Weak solutions of alkalies and lime water pro-

[1] Indigo, or its derivatives, appears to be a product of animal metabolism, and is secreted by a number of organs. It has been detected in the dark "pin heads" which form in the perspiration glands of the skin. Both indol and skatol are present in the gaseous excrement, being formed in the intestines.

[2] Schunck has described the following process for the preparation of indican: Dried woad leaves are finely powdered and extracted with alcohol by percolation. A little water is added, and the solution concentrated as quickly as possible at the ordinary temperature in a current of air. The residual brown liquid is filtered from the green residue of fat and coloring matter, and agitated with some freshly precipitated cupric hydroxide. The liquid is filtered, the copper precipitated by sulphuretted hydrogen, and the liquid again filtered. The filtrate, which should be light yellow, is concentrated to a syrup at the ordinary temperature in a current of air, treated with cold alcohol to remove decomposition-products, filtered, and mixed with twice its measure of ether. The filtered liquid yields on evaporation a clear brown syrup consisting of pure indican.

duce a bright yellow color. The alcoholic solution of indican gives a bright yellow precipitate with lead acetate, which is increased on adding ammonia; but the aqueous solution does not give this reaction. Indican is soluble in ether, but is extracted by water from its ethereal solution.

The most characteristic and important property of indican is the behavior of its solution with dilute acids, by the action of which it splits up with formation of i n d i g o t i n or indigo-blue, i n d i r u b i n, and i n d i g l u c i n. The reaction occurs slowly in the cold, but rapidly at a boiling heat, the liquid becoming first sky-blue, then opalescent, and finally purple, and on cooling a purple deposit of mixed indigotin and indirubin is obtained (both of which may be obtained in a crystalline state by sublimation), while indiglucin remains in solution. The following formula represents the formation of indigotin from indican:—

$$\underset{\text{Indican.}}{C_{26}H_{31}NO_{17}} + 2H_2O = \underset{\text{Indigotin.}}{C_8H_5NO} + \underset{\text{Indiglucin.}}{3C_6H_{10}O_6.}$$
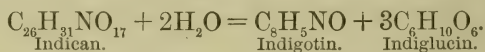
INDIGO BROWN. If an aqueous solution of indican be boiled or heated for some time it undergoes a change, and on now treating it with an acid it yields neither indigotin nor indirubin, but dark-brown or blackish flocks, consisting of a mixture of two brown resinous bodies, called by Schunck i n d i r e t i n and i n d i h u m i n, of which only the latter is soluble in alcohol, and to which bodies he attributes the formula $C_{18}H_{17}NO_{10}$ and $C_8H_8NO_5$ respectively.

Leucine, $C_6H_{13}NO_2$, a body produced in the putrefaction of cheese, and by the treatment of various animal substances with sulphuric acid, is also a product of the reaction of dilute acids on indican.

Indirubin or Indigo Red, C_8H_5NO, is obtained with indigotin by the decomposition of indican, especially when oxalic or tartaric acid is used.[1] It may be separated from the indigotin by boiling the precipitate with alcohol.[2] On concentrating and cooling the alcoholic solution, the indirubin is obtained in long red crystals, insoluble in caustic alkalies, but reducible by boiling with an

[1] Indigo red may be prepared synthetically by boiling 5 gm. of indophor with one litre of water until no more carbon dioxide is evolved. The solution is filtered, mixed with a hot solution of 4 gms. of isatin in one litre of water, and a small amount of a solution of carbonate is added. The dyestuff separates out in small red needles.

[2] The amount of indirubin present in commercial indigo varies from 1 to 8 per cent.

alkali and stannous chloride or glucose to a l e u c o - d e r i v a t i v e, the solution of which on exposure to air yields purple flakes, which when washed, dried, and heated, give a sublimate of beautiful needles, readily soluble in boiling alcohol, and recrystallizing as the solution cools.[1] If a piece of calico be immersed in a reduced alkaline solution of indirubin, and then exposed to the air, it becomes dyed a fast purple color (not blue as with indigotin) which is not affected either by acids or soap.   Indirubin dissolves in cold concentrated sulphuric acid with beautiful purple color. On heating the solution it becomes lighter and gives off a little sulphur dioxide.   On diluting the solution of indirubin in sulphuric acid with water, a liquid is obtained which dyes cotton, wool, and silk a fine purple color.   Indirubin is not affected by boiling with dilute sulphuric acid and potassium bichromate, a character which distinguishes it from indigotin.

INDIGLUCIN, $C_6H_{10}O_6$, is obtained from the liquid from which the above coloring matters have been separated, by adding excess of lead acetate, filtering, and treating the filtrate with excess of ammonia.   The bulky yellow precipitate thus obtained is decomposed by sulphuretted hydrogen, and the indiglucin purified by repeating the process or treatment with animal charcoal.   On concentrating the colorless liquid or syrup, and adding alcohol and two volumes of ether, the indiglucin separates as a pale yellow, sweetish syrup, which turns red and blackens when heated with sulphuric acid, and yields oxalic acid on treatment with nitric acid.   It reduces hot Fehling's solution and silver nitrate.   The solution gives no precipitate either with neutral or basic lead acetate, unless ammonia be added.   If milk of lime be added and the solution filtered, a strongly alkaline liquid is obtained, and on boiling this it becomes thick from the formation of a flocculent yellow precipitate, which completely redissolves to a clear yellow solution on cooling.   This reaction may be repeated indefinitely.   By fermentation with yeast, indiglucin appears to yield a c e t i c a c i d.

Indigotin.   INDIGO BLUE. C_8H_5NO or $C_{16}H_{10}N_2O_2$.   This substance probably has the constitution represented by the following formula:[2]—

$$C_6H_4: \left\{ \begin{matrix} CO \\ NH \end{matrix} \right\} : C : C : \left\{ \begin{matrix} CO \\ NH \end{matrix} \right\} : C_6H_4.$$

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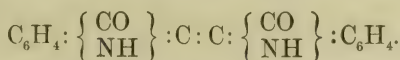
[1] Indirubin may be prepared from *indophor*, which consists of indoxyl carbonic acid.   When this substance is heated with water until no more CO_2 is evolved, filtered hot, and the filtrate treated with caustic soda, indirubin is formed.

[2] Baeyer regards the molecule of indigotin as composed of two symmetrical

Indigotin is the constituent on which the value of commercial indigo depends.

Pure indigotin may be obtained by mixing one part of commercial indigo in fine powder with two parts of plaster of paris, making the whole into a paste with water, and spreading it on an iron plate. When quite dry the mass is cautiously heated, when the surface becomes covered with beautiful crystals of pure indigotin, which may be removed with a fine spatula. Indigotin may also be obtained in a pure state by the oxidation of i n d i g o - w h i t e, $C_{16}H_{12}N_2O_2$, or i n d o x y l i c a c i d, $C_9H_7NO_3$, or by the reduction of o r t h o n i t r o-p h e n y l-p r o p i o l i c a c i d. It may also be prepared by heating i s a t i n, $C_8H_5NO_2$, with a mixture of phosphorus trichloride and pentachloride, and reducing the resultant i s a t i n c h l o r i d e, C_8H_4NOCl, by ammonium sulphide.

Pure indigotin forms dark blue crystals exhibiting a coppery reflection and having the form of a right rhomboidal prism. In the form of powder it is deep blue, and assumes a coppery lustre when burnished. Its specific gravity is 1.35. Indigotin is not fusible, but sublimes at about 290° C., with more or less decomposition. In an inert gas it may be volatilized unchanged.

Indigotin is unchanged in the air at ordinary temperatures, and has neither taste nor smell. It is insoluble in hot or cold water, cold alcohol, ether, and fatty and essential oils. Creosote, carbolic acid, absolute alcohol, amylic alcohol, and carbon disulphide dissolve a little indigotin when hot, but it is again deposited on cooling. Its best solvents are glacial acetic acid, nitrobenzene, and aniline. On boiling powdered indigo with aniline it readily dissolves to form a blue solution, which if filtered hot and allowed to cool deposits nearly all the indigotin in beautiful crystals, which after being washed with alcohol are perfectly pure. Boiling paraffin and high boiling petroleum are also solvents of indigotin. The dilute solutions have the color of an alcoholic solution of magenta.

If a little finely powdered indigotin be treated with glacial acetic acid and one or two drops of strong sulphuric acid added, a deep blue solution is formed, from which the indigotin is precipitated unchanged on dilution with water. If any fibre be immersed

halves, $C_6H_4\left\{\begin{matrix} CO \\ NH \end{matrix}\right\}C$:, and this half-molecule he calls i n d o g e n. The indogenides are compounds of yellow or bluish-red color, and some of them yield blue salts which exhibit the indigo spectrum.

in the undiluted solution, and then washed with water, it will be dyed blue.

Indigotin is a perfectly neutral substance, and is insoluble in dilute acids and alkalies.

When subjected to dry distillation, either alone or in admixture with an alkali, indigotin yields a n i l i n e, C_6H_7N.

When subjected to the action of oxidizing agents, such as dilute nitric acid, chromic acid, or chlorine, indigotin is converted, in the presence of water, into a body called i s a t i n [1] or i n d i g o t i c a c i d.

[1] ISATIN, $C_8H_5NO_2 = C_6H_4 \left\{ {.CO. \atop .N:} \right\} C(OH)$. This body is obtained by oxidizing indigo by chromic acid, or preferably nitric acid. Powdered indigo is made into a thin paste with water, the mixture heated to the boiling point, and the nitric acid added cautiously till the blue color disappears, when the whole is largely diluted with boiling water and the liquid filtered. Impure isatin separates on cooling, and is washed with ammoniacal water. Isatin forms deep yellowish-red prismatic crystals, sparingly soluble in cold water, but freely in boiling water and in alcohol. The solution stains the skin yellow, and gives it a disagreeable odor. When heated, isatin melts and sublimes, with partial decomposition. It forms crystalline compounds with the acid sulphites of the alkali-metals, and dissolves in alkalies to form violet solutions, which turn yellow when heated and then contain a salt of i s a t i c a c i d. H y d r i n d i c a c i d or d i o x i n d o l is formed by the action of sodium amalgam on this solution. Further reduction in acid solution produces o x i n d o l, and this when distilled with zinc-dust yields i n d o l, a weak base existing in human excrement. The relationship of these bodies to indigotin, isatin, and each other is shown by the following constitutional formulæ :—

Hydrindigotin, ... $C_6H_4 \left\{ {.CO. \atop .NH.} \right\} CH.HC \left\{ {.CO. \atop .NH.} \right\} C_6H_4$

Indigotin, ... $C_6H_4 \left\{ {.CO. \atop .NH.} \right\} C:C \left\{ {.CO. \atop .NH.} \right\} C_6H_4$

Isatin, ... $C_6H_4 \left\{ {.CO. \atop .N:} \right\} C(OH)$

Isatic acid, ... $C_6H_4 \left\{ {.CO.CO.OH \atop .NH_2} \right.$

Dioxindol, ... $C_6H_4 \left\{ {.CH(OH). \atop .NH.} \right\} CO$

Oxindol, ... $C_6H_4 \left\{ {.CH_2. \atop .NH.} \right\} CO$

Indol, ... $C_6H_4 \left\{ {.CH: \atop .NH.} \right\} CH$
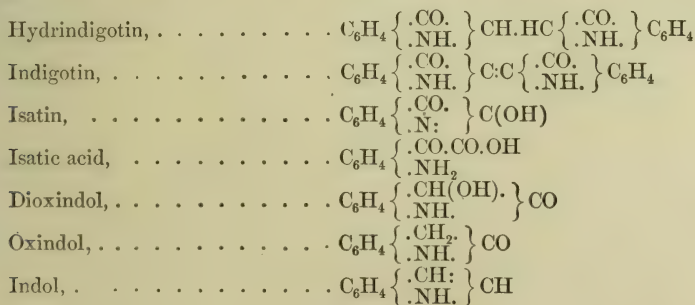
Silver nitrate throws down from alkaline solutions of isatin a red precipitate containing $C_8H_4AgNO_2$. The hydrogen of the hydroxyl group may also be replaced by acid radicals, as in a c e t y l - i s a t i n, $C_8H_4(C_2H_3O)NO_2$. M o n o - and d i - c h l o r - and b r o m - i s a t i n s are obtained by the action of chlorine and bromine on isatin or moist indigo. I s a t i n - s u l p h o n i c a c i d, $C_8H_4(SO_3H)NO_2$, is formed by the treatment of indigotin-sulphonic acid by permanganate or other oxidizing agents in acid solution. It is soluble, and difficultly crystallizable.

Hot and strong nitric acid converts indigo-blue into p i c r i c and
n i t r o s a l i c y l i c   a c i d s, some carbonic or oxalic acid being
simultaneously formed.

Indigo White. HYDRINDIGOTIN. REDUCED INDIGO. $C_{16}H_{12}N_2O_2$.
When indigotin is subjected to the action of reducing agents it
assimilates two atoms of hydrogen, forming a leuco-body of the
above composition, the constitutional formula of which is prob-
ably:—

$$C_6H_4 \left\{ \begin{array}{c} CO \\ NH \end{array} \right\} CH.HC \left\{ \begin{array}{c} CO \\ NH \end{array} \right\} C_6H_4$$

A great variety of substances have the power of reducing indigo-
blue to indigo-white. Thus in alkaline solution, or presence of
free alkali, we may use:—sodium amalgam; zinc, tin, aluminium,
and phosphorus; ferrous hydroxide; phosphorous, hypophos-
phorous, and hyposulphurous (Schützenberger's) acids; certain
phosphides, arsenides, and sulphides (especially sulphide of
arsenic); glucose, gallic acid, the butyric ferment, etc. The re-
sultant reduced indigo is soluble in the alkaline liquid. In acid
solutions, indigotin is reduced less readily, hyposulphurous acid
(H_2SO_2) being almost the only available agent.[1]

Indigo-white is a grayish-white, amorphous, tasteless, odorless
substance, having a silky lustre. Heated out of contact with the
air a small quantity of indigotin sublimes, and a carbonaceous
mass is left. In contact with the air at the ordinary temperature
white indgo gradually becomes blue from oxidation, and the action
is rapid in presence of moisture. Indigo-white is insoluble in
water and dilute acid liquids, but dissolves in alcohol and ether.

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[1] A convenient process for the preparation of white indigo consists in treating 1
part of indigo-blue with 3 parts of crystallized ferrous sulphate, 3 parts of slacked
lime, and 20 of water in a closed vessel. The mixture is agitated at intervals for
some days, and finally allowed to settle. The pale yellow liquid is then syphoned
off into a bottle filled with carbon dioxide, containing some recently boiled hydro-
chloric acid. The indigo-white is immediately precipitated, and when the bottle
is quite full it is immediately closed. After standing some time the liquid is
filtered in an atmosphere of carbon dioxide or coal-gas, the precipitate washed
with air-free cold water, and dried *in vacuo*.

An alterative process is to treat the indigo-blue with caustic soda and glucose,
the subsequent operations being the same as those already described. An instan-
taneous reduction may be effected by treating the finely powdered indigo with a
solution of a hyposulphite, obtained by agitating zinc-dust with a strong solution
of acid sulphite of sodium, and treating the decanted liquid with excess of
caustic soda.

Hydrindigotin is soluble in solutions of the alkalies and alkaline earths, but its acid characters are very feebly marked, for the presence of a textile fabric suffices to decompose its compounds, the indigo-white uniting with the fibre and alkali being set free.[1] The alkaline solutions of reduced indigo have a yellow tint, but in contact with air they become green and blue and covered with a bronzy scum, and deposit minute crystals of indigotin. Addition of an oxidizing agent produces the same effect more rapidly, and even a slight rise of temperature causes a similar change. The application of indigo in dyeing by the vat-process is based on its reduction to white indigo, the solubility of the reduced substance in alkaline liquids, and its reoxidation to indigo-blue on exposure to air.[2] Alkaline solutions of hydrindigotin give bulky white precipitates with solutions of magnesium, zinc, aluminium, lead, ferrous, manganous, and stannous salts. The last precipitate is employed for printing indigo on fabrics. When heated it yields metallic tin and a sublimate of indigotin.

Concentrated sulphuric acid dissolves white indigo with intense purple coloration, forming m o n o - and d i - i n d i g o t i n - s u l - p h o n i c a c i d s.

INDIGOTIN-MONOSULPHONIC ACID. SULPHOPURPURIC ACID. Indigo-purpuric Acid. $C_{16}H_9N_2O_2.SO_3H$. This body, also called s u l p h o p h e n i c i c a c i d, may be obtained by adding one part of good commercial indigo in fine powder to four parts of concentrated sulphuric acid, and heating the mixture for a short time, or until a sample gives a deep blue color when largely diluted with water. Too high a temperature and too prolonged heating must be carefully avoided, or the disulphonic acid will be produced. As soon as the product is found to be soluble, the mass is thrown into about fifty parts of water, when a beautiful purple precipitate of sulphopurpuric acid will be thrown down. This is filtered off, and washed slightly with dilute hydrochloric acid.

Sulphopurpuric acid is almost insoluble in dilute acids and very sparingly soluble in water, but communicates a bluish-purple color to the liquid. On adding sodium carbonate or acetate to the aqueous solution, purple flocks of the s o d i u m s u l p h o p u r -

[1] White indigo forms two compounds with lime, one of which is soluble and the other insoluble.

[2] A certain amount of indigotin is, however, never recovered ; the cause of the loss is obscure, and its investigation would probably lead to means of preventing it which would well repay the trouble.

p u r a t e, $C_{16}H_9N_2O_2.SO_3Na$, are precipitated. This salt is soluble in a large quantity of water, and is employed in dyeing under the name of *indigo-purple* or *red indigo-carmine*. Precipitates are produced by solutions of calcium, aluminium, and iron. Caustic alkalies produce no effect, but the solution is decolorized by reducing agents, such as zinc, sulphuretted hydrogen, or stannous chloride, and becomes blue again on exposure to the air.

INDIGOTIN-DISULPHONIC ACID. SULPHINDIGOTIC ACID. $C_{16}H_8N_2O_2$ $(SO_3H)_2$. This acid, also called i n d i g o-s u l p h u r i c a c i d and s u l p h i n d y l i c a c i d, is obtained when the monosulphonic acid is heated with eight or ten parts of sulphuric acid, and hence is usually formed, to a greater or less extent, together with the monosulphonic acid, when indigo is treated with concentrated sulphuric acid. It forms the sole product when the sulphuric acid amounts to fifteen times the weight of the indigo employed. It is best obtained by carefully heating the finely pulverized commercial coloring matter, or preferably pure indigotin, with ten or twelve parts of ordinary strong sulphuric acid (sp. gr. 1.845), or six or seven parts of the fuming acid, to a temperature of 50° C. for several hours, or until a small sample is found to be entirely soluble in water. The product is then cooled and treated with about fifty parts of water. On standing for some time, any monosulphonic acid and certain other impurities will be deposited, and the filtered solution will be pure blue.[1] To prepare pure sulphindigotic acid, clean white wool or flannel, which has been previously thoroughly washed by boiling with soap and solution of carbonate of sodium and then with pure water, is immersed in the solution till the greater part of the coloring matter is taken up. It is then well washed to remove the free sulphuric acid, and stripped by immersing it in a weak solution of ammonium carbonate. The blue solution thus obtained is evaporated at a temperature not exceeding 50° C., and the residue treated with rectified spirit to dissolve any hyposulphindigotate. The undissolved portion, consisting of ammonium sulphindigotate, is treated with water, the solution precipitated by lead acetate, and the insoluble lead salt washed and decomposed by sulphuretted hydrogen. A colorless solution of hydrindigotin-disulphonic acid, $C_{16}H_{10}N_2O_2$-$(SO_3H)_2$, results; and on exposure to air this readily oxidizes to a

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[1] A third acid, called h y p o s u l p h i n d i g o t i c a c i d, is said to be formed, but no formula has been assigned to it. In its reactions it closely resembles sulphindigotic acid, but its salts are soluble in rectified spirit.

blue solution of sulphindigotic acid, which may be obtained as a blue amorphous mass by evaporating the solution.

Sulphindigotic acid is decolorized by reducing agents. By oxidizing agents it is converted into isatin-disulphonic acid, $C_{16}H_8N_2O_4(SO_3H)_2$, a body of an orange color, on the formation of which several methods for the assay of commercial indigo are based.

Sulphindigotic acid is decomposed by an excess of strong caustic alkali, with production of a yellow liquid; but with dilute alkalies it reacts to form sulphindigotates.[1] These salts, when solid, have a beautiful bronze-blue color, and dissolve freely in pure water, yielding blue solutions. In saline solutions they are almost or quite insoluble; and hence, on adding common salt or sulphate of sodium to the solution of a sulphindigotate of alkali-metal, the latter compound is precipitated in blue flakes.

Potassium sulphindigotate, $C_{16}H_8N_2O_2(SO_3K)_2$, is soluble in 140 parts of water, and the sodium salt somewhat more readily. The lead salt is insoluble, and the barium salt very slightly soluble in cold, but more readily in hot water. The sulphindigotates of calcium, magnesium, and aluminium are easily soluble.

Indigo Extract. Soluble Indigo. Indigo-carmine. These names are applied in commerce to more or less pure indigo-sulphonic acids and their salts. The exact nature of the product varies considerably with the quality of the indigo, the proportion of sulphuric acid used, the temperature employed in the process, and the subsequent treatment of the sulphonated indigo. With a moderate proportion of acid, the mono-sulphonic acid is the chief product, and this, when converted into the sodium salt, is known as *indigo-purple* or *red indigo-carmine.* A product of similar composition, known as *Boiley's blue,* is prepared by gradually adding 1 part of finely powdered indigo to 10 or 20 parts of sodium hydrogen sulphate, $NaHSO_4$, in a state of fusion. The product is dissolved in water, precipitated with common salt, and washed with brine. Boiley's blue is a crystalline, light purplish mass, soluble in water with beautiful blue-violet color. Its solution in strong boiling acetic acid deposits, on cooling, large prismatic crystals, exhibiting a coppery reflection. It is insoluble in alcohol or

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[1] The blue color of solutions of indigo-sulphonic acid is not affected by alkaline carbonates, but as caustic alkalies change the color to yellow, the latter may be determined in the presence of the former by the use of sulphindigotic acid as an indicator.

ether, but readily soluble in hot water. The light transmitted by the solution is red. With barium and strontium salts it yields violet precipitates.

Saxony blue, chemic, chemic blue, and *sour extract* are names applied to the solution of indigo in sulphuric acid, without any neutralization or subsequent treatment. It is not unsuitable for wool-dyeing, as the green coloring matter which it generally contains has no affinity for the wool-fibre; but for dyeing silk this must be removed. For this purpose the acid is usually converted into a sodium salt, known as *indigo-carmine.* This can be made by neutralizing the acid with soda-crystals, when the sodium sulphate simultaneously formed precipitates the sodium sulphindigotate, the separation being rendered complete by adding common salt. The precipitate may be purified by re-solution in water, and again salting out, the process being repeated until the absence of a green tint in the filtered liquid shows that the objectionable green coloring matter has been entirely removed. The purified precipitate should then be washed with water until the liquid begins to run through blue, when it is drained and pressed. In some cases the solution of the sulphonated indigo is at once precipitated with common salt, without being previously neutralized. Magnesia and chalk are sometimes employed instead of soda-crystals. The potassium salt, obtained by precipitating a solution of sulphindigotic acid by potassium acetate, is occasionally met with.

Indigo-carmine occurs in commerce as a dry powder or copper-colored masses having a blue streak, and also as a blue or purple paste, which should be free from any green or brown reflection. The following figures indicate the usual percentage composition of indigo pastes:

	ORGANIC MATTER.	SALINE MATTERS.	WATER.
Best quality	12.4	13.9	73.7
Second quality	10.2	4.8	85.0
Third quality	4.96	5.70	89.34
No. 1	10.8	4.7	84.5
No. 2	5.6	4.7	89.7
No. 3	9.55	7.80	82.65

The *water* is determined by drying 2 grammes of the sample at

100°, and noting the loss of weight. The dried substance is then heated just to redness in platinum, when the residue represents the *saline matters*, the loss being regarded as *organic matter*. The figure thus obtained is sometimes reported as "coloring matter," but in reality is made up of water not driven off at 100°, sulphuric acid evolved from $NaHSO_4$, organic impurities of the indigo, &c. As the real coloring matter of indigo-carmine usually ranges from 2 to 5 per cent., with an average of about 3 per cent., it is evident that the organic matter of a sample does not, even approximately, indicate its tinctorial value. The indication is still more worthless in presence of *dextrin* and other adulterants. A useful method of assaying indigo-carmine is to dissolve 1 gramme of the sample in a litre of water, and compare the depth of color with that yielded by a standard specimen; but the difference in the shade of various makes of indigo-paste often renders this method of examination untrustworthy. In such cases the true strength of the sample is best ascertained by titration with permanganate or hyposulphite.

The presence of the green coloring matter in indigo-paste may be detected by rubbing a little of the coloring matter on glazed paper. On drying, the shade will vary from pale blue to a rich coppery-purple, according to the mode of manufacturing the paste; and if any green coloring matter be present, a green border will be observed surrounding the blue circle. The test may be modified by dropping an aqueous solution of the coloring matter on a piece of filter-paper, when the green margin will become evident as the paper dries.

Indigo-extracts should leave no undissolved gritty particles when treated with water, but all the common varieties leave a dirty greenish-black insoluble residue. Soluble indigo is said to be sometimes adulterated with farina, dextrin, and other inert matters. A general indication of the quality of the sample may be obtained by dissolving a known weight in water, adding a little alum and cream of tartar, and then introducing successive swatches of well-washed white wool or flannel. The value of the sample will be in proportion to the weight of wool dyed to a standard shade of color. The green coloring matter already referred to as occurring in some qualities of soluble indigo is taken up by wool last, or not at all, when the sample is thus treated.

The more acid varieties of soluble indigo are employed for dyeing wool and worsted. The neutral is employed for silk, and

is also used for dyeing mixed goods containing cotton, and for printing woolen goods, such as tapestry-carpets, etc. The dyeing is effected in an acid bath, to which cream of tartar, sodium sulphate, or alum is sometimes added.[1]

Synthetic or Artificial Indigo. Ever since 1870 when Bæyer produced indigotine by treating isatin with a mixture of phosphorous trichloride and acetyl chloride, the attention of chemists has been fixed on the problem of producing synthetic indigo at a price sufficient to compete commercially with the natural product. Since that time numerous syntheses have been proposed for indigo, but it has only been during the past few years that the artificial product has been able to enter into commerce.

The first step in the preparation of indigo was the formation of I n d o l. This substance possesses the formula:
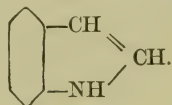
It was first prepared by Bæyer by the reduction of indigotine; Nencki also obtained it by the pancreatic fermentation of albumen. Subsequently it has been prepared synthetically by a number of reactions: by heating orthonitrocinnamic acid with potash and iron filings; by the condensation of diethylorthotoluidine; by melting carbostyril with caustic potash; by distilling nitropropenylbenzoic acid with lime; by heating ortho-amidostyrol with sodium ethylate; by the condensation of tetrahydroquinoline; by the action of zinc dust and ammonia on orthonitrophenyl acetaldehyde; and substituted indols are prepared by heating hydrazones with zinc chloride (Emil Fischer). By the oxidation of indol by means of ozone, Nencki prepared artificial indigo (*Ber.* viii., 727).[2]

Bæyer (in 1878) showed that o x i n d o l was an inner anhydride of orthoamidophenylacetic acid; he also prepared isatin from oxindol, and as indigo had already been prepared from the former substance, a complete synthesis of indigo from orthoamidophenylacetic acid was effected. Indigo has also been synthetically

[1] A solution of indigo-carmine may be used as an indicator in the estimation of nitrites and chlorine, both of which decolorize it on boiling. It is also employed in the estimation of oxygen and tannin and as a test for sugar in urine, as sugar changes the blue color of indigo-carmine paper to yellow.

[2] Emmerling and Engler, in 1870, claim to have prepared indigo by heating nitro-acetophenone with zinc dust and soda-lime.

prepared from orthonitrocinnamic acid (*Ber.* xiii., 2259); from orthonitropropiolic acid (*Annal.* cxliii., 325, cxlvii., 78, cliv., 137); from orthonitrobenzaldehyde, and analogous substances. If phenylglycocine is treated with fuming sulphuric acid indigo-disulphonic acid is obtained, and the yield is quite satisfactory. Pure indigo may also be obtained from phenylglycocine by heating it with four times its weight of caustic soda until the pale yellow melt at first obtained becomes pure orange in color; on treating this with a large amount of water indigo separates out (L e d e r e r, *J. prakt. Chem.* xlii., 383). H e u m a n n (*Chem. Zeit.* xiv., 1367) has prepared indigo by heating phenylglycocoll, $C_6H_5.NH.CH_2.COOH$, with caustic soda until the melt becomes dark orange in color; on dissolving the product in water and passing air through the solution, pure indigo is deposited. If the melt obtained by heating aniline and monochloracetic acid with caustic soda until the mass is yellow, is dissolved in water and a current of air is passed through the solution, pure indigo is precipitated. Anilidoacetic acid may also be used with the same results. By heating anilidomalonic esters to 200° C. or above an inner condensation takes place, and an indoxylic ester is the result; this on hydrolysis yields indoxylic acid, (the so-called I n d o p h o r,

$$C_6H_4 \begin{cases} (1)C.OH \\ (2)NH \end{cases} > C.CO_2H),$$ and indigo may be prepared from the

latter by oxidizing with a current of air in an alkaline solution. Another synthesis is by condensing orthonitrotoluene with oxalic ester, and reducing the orthonitrophenylpyrouvic acid so obtained with sodium amalgam, allowing the product to stand in concentrated sulphuric acid and subsequently saturating with ammonia and oxidizing by means of a current of air. The indigo obtained in this way is about 23 per cent. of the nitrophenyl-pyrouvic acid employed.

The Badische Anilin und Soda Fabrik of late have been placing synthetic indigo upon the market in large quantities under the name of i n d i g o - p u r e partly as paste and partly as powder. This dyestuff contains about 97 per cent. of pure indigotine and 3 per cent. of moisture and mineral substances. The successive stages in the manufacture of this product may be outlined as follows: Naphthalene, $C_{10}H_8$, is converted into phthalic acid, $C_6H_4 \begin{cases} COOH \\ COOH \end{cases}$, this into phthalimide, $C_6H_4 \begin{cases} CO \\ CO \end{cases} > NH$, the latter

into anthranilic acid, $C_6H_4 \begin{Bmatrix} COOH \\ NH_2 \end{Bmatrix}$, this into phenylglycine

orthocarboxylic acid $C_6H_4 \begin{Bmatrix} COOH \\ NH.CH\ COOH \end{Bmatrix}$, which is then con-

verted into indoxylcarboxylic acid, $C_6H_4 \begin{Bmatrix} CO \\ NH \end{Bmatrix} > CH\ COOH$ and

finally into indigo, $C_6H_4 \begin{Bmatrix} CO \\ NH \end{Bmatrix} > C : C < \begin{Bmatrix} CO \\ NH \end{Bmatrix} C_6H_4$.

The INDIGO-SALT (of Kalle & Co.) is prepared from ortho-nitrobenzaldehyde by heating with acetone and then combining the product with sodium bisulphite. This substance has the formula:

$$C_6H_4 \begin{Bmatrix} (1)\ CH(OH).CH_2.C(OH) \begin{Bmatrix} CH_3 \\ SO_3Na \end{Bmatrix} + 3H_2O \\ (2)\ NO_2 \end{Bmatrix}$$
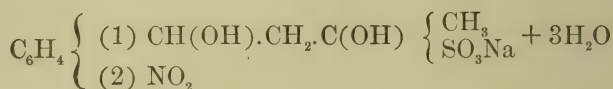
It is a white crystalline paste which smells of sulphurous acid; when heated with caustic soda it is decomposed, and indigo is slowly deposited. It is applied to cotton and wool by impregnating the fibre with a solution of the dyestuff, and after drying, passing through a solution of caustic soda which liberates the indigo on the fibre. In calico-printing indigo has also been produced upon the fibre by printing with propiolic acid and reducing with xanthogenate of sodium. The colors thus obtained are said to be brighter than natural indigo and are more resistant to rubbing and soaping; however, propiolic acid cannot be used in connection with steam colors, and the xanthogenate of sodium, which appears to be the most suitable reducing agent for the purpose, gives the material a disagreeable odor.

From the fact that artificial indigo consists of pure indigotine and does not contain any indigo-red (indirubin) or indigo-gluten, it does not appear to give as good results as the natural product in cotton dyeing. This defect may be remedied, however, by adding to the vat such substances as glue, Turkey-red oil, etc.; or better, by impregnating the cotton with these before dyeing.

Commercial Indigo.—Indigo occurs in commerce in lumps or fragments of a deep blue color, usually showing a bronze or purple-red streak when rubbed with any hard substance, or, in the case of the better kinds, even with the friction of the thumb only. The fracture of indigo is dull and earthy, and it is practically insoluble in water or any of the ordinary solvents, except concentrated sulphuric acid.

Indigo varies much in quality according to the care taken in its preparation.[1] The i n d i g o t i n or indigo-blue, which is the most valuable and abundant constituent, varies from 20 to (occasionally) 80 per cent., with an average of about 45 per cent. The only other constituent of tinctorial value is the i n d i r u b i n or i n d i g o - r e d, the proportion of which is generally between 3 and 5 per cent. C h l o r o p h y l l (more or less altered), a brown coloring matter called i n d i g o - b r o w n, and a gluten-like substance termed i n d i g o-g l u t e n, are the other principal constituents, in addition to a trifling percentage of m o i s t u r e and a variable proportion of m i n e r a l m a t t e r.

When an indigo of superior quality is required, as is desirable for making indigo-extract, the finely powdered substance is treated several times at a gentle heat with hydrochloric acid containing a little free chlorine, by which treatment iron, lime, and some other mineral impurities are dissolved, while the amylaceous matters are converted into dextrin or sugar, which is removed by subsequent washing with water. The residue is then treated with weak caustic soda, which removes chlorophyll and some other organic impurities. The product is known in commerce as *refined indigo*. The same name is applied commercially to a product obtained by reducing finely-ground indigo with ferrous sulphate and lime.

The technical analysis of indigo is usually limited to determinations of the m o i s t u r e, a s h, s p e c i f i c g r a v i t y, and c o l o r- i n g m a t t e r. In some cases the i n d i g o t i n is the only coloring matter taken into account, but the i n d i r u b i n ought not to be neglected, as it modifies the shade of the blue produced, and is itself capable of dyeing any fast colors. Indigo-brown, on the other hand, is of no practical interest, as in the dye-vat it forms an insoluble compound with the lime used, and in making extract is precipitated when the sulphuric acid solution of the indigo is diluted with water. The methods of determining the proportion of coloring matter in indigo are very numerous, but few can be at once considered both accurate and practical.[2]

The *moisture* in commercial indigo usually ranges from 3 to 8

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[1] See a paper on West African Indigo by R a w s o n and K n e c h t, in the *Jour. Soc. Dyers, &c.*, iv, 66.

[2] The valuation of indigo has been treated in an exhaustive manner by C. R a w s o n (*Jour. Soc. Dyers, &c.*, i, 74, 211), from whose paper much of the information here given is derived, and to whom the author is indebted for the perusal and correction of this article on the subject.

per cent., and may be determined with accuracy by observing the loss of weight undergone by the sample on exposure to the temperature of boiling water.

The *ash* left on igniting commercial indigo is a useful criterion of its purity. In the purest kinds it is sometimes as low as 2 per cent., but from 5 to 8 per cent. is a more usual proportion. Some of the inferior kinds of indigo, such as Kurpah and Madras, frequently contain from 25 to 35 per cent. of ash.

L e u c h e s has recommended the determination of the *specific gravity* as a useful preliminary test of the quality of indigo, and gives the following figures in illustration of the relation between the specific gravity and percentage of indigotin:—

| Specific gravity . . | 1.324 | 1.332 | 1.350 | 1.371 | 1.384 | 1.421 | 1.437 | 1.455 |
| Indigotin, per cent. | 56 | 55 | 53 | 49 | 44 | 40 | 37 | 35 |

H e l e n C o o l e y (*Amer. Jour. Anal. Chem.*, ii, 130) has recorded the specific gravities and percentages of ash and indigotin contained in the following samples of commercial indigo:—

DESCRIPTION.	SPECIFIC GRAVITY.	ASH.	INDIGOTIN.
Kurpah blue, ...	1.129	17.54	55.11
Watson's best, . . .	1.292	6.50	59.53
Bengal red, ...	1.391	6.41	54.03
Oude, ...	1.427	7.02	52.90
Bengal blue, ...	1.431	7.50	57.60
Kurpah red, ...	1.529	21.20	45.28
Guatemala, ...	1.559	14.49	47.04

These figures do not establish the value of the specific gravity as a test of quality, or even indicate that it is a criterion of the proportion of ash.

Starch, sometimes colored with iodine, is said to be occasionally employed for adulterating indigo. To detect it, the sample should be treated with a cold dilute solution of sodium thiosulphate, and the insoluble residue washed with proof spirit. The starch-granules may then be detected by the microscope, or the residue may be boiled with water and the starch tested for by adding iodine solution to the filtered liquid.

A useful *proximate analysis* of indigo, together with a moderately

accurate determination of the indigotin present, may be effected as follows:—The sample is dried at 100° to determine the water, then treated with hot water and the residue dried and weighed. This gives the matters soluble in water, and the residue is treated in succession with dilute hydrochloric acid, dilute caustic soda, and alcohol. The loss of weight resulting from each of these treatments may be determined with advantage, especially the amount of matter soluble in alcohol, as this represents the *indigo-red* of the sample.[1] The residue after this treatment is dried and weighed. Its weight, after deducting that of any ash it may leave on ignition, represents the *indigotin* of the sample.

C. Tennant Lee (*Chem. News*, 1, 49; from *Jour. American Chem. Soc.*) has proposed to assay indigo by observing the amount of indigotin which can be obtained by sublimation—a method which is easy, rapid, and, in his experience, uniformly satisfactory. For the operation he recommends the use of a shallow, flat-bottomed, platinum tray, 7 centimetres in length, 2 wide, and 0.3 or 0.4 deep. About 0.25 gramme of the finely powdered sample, previously dried at 100°, is introduced and spread evenly over the bottom of the tray, which is then gradually heated on an iron plate. When the surface of the indigo becomes covered with a shining layer of crystals, the tray is covered with a piece of sheet iron, about 8 or 9 centimetres in length and bent into a slightly arched form, so that the highest point may be about 1 cm. above the plate. The heat is simultaneously lowered. Purple vapors of indigotin are now given off, a portion condensing on the concave side of the arch. The heat is now raised slowly, so as to maintain a constant sublimation of indigotin, the progress of which can be observed by raising the arch. With a 50 per cent. indigo, the operation is complete in 30 to 40 minutes; but soft Java indigo must be treated with more caution, the sublimation sometimes occupying two hours. When all crystals of indigotin have disappeared from the dark-colored surface of the residue, the tray is removed, cooled in a desiccator, and weighed, the loss of weight being regarded as *indigotin*. On repeating the process the results should not vary more than 0.3 per cent. C. Rawson points out that the author of the above process has not given any figures by

[1] As indigo-brown is only with difficulty removed by treating indigo with caustic soda, the indigo-red is liable to be contaminated with the portion of the brown which escaped solution. By treating the impure product with dilute caustic alkali, the indigo-brown will be readily dissolved and the indirubin obtained pure.

which the results obtained can be compared with those yielded by
other methods. In his own experience he has found the agree-
ment to be in many cases very good; but, as a rule, inferior quali-
ties of indigo, containing much matter soluble in hydrochloric acid,
yield by the sublimation-process results above the truth; whilst,
on the other hand, rich samples give results which are undoubtedly
too low. Rawson obtained differences of upwards of 2 per cent.
by an alteration in the cover. It seems probable that these
strictures are justified, but that the process is nevertheless very
useful in many cases. If applied to indigo which had been sub-
jected to a preliminary treatment with dilute hydrochloric acid,
and then thoroughly dried, it would probably yield, on subjection
to carefully-regulated sublimation, results of considerable accuracy.

Another method of estimating the real indigotin present in com-
mercial indigo is based on its reduction to the leuco-derivative
(white indigo), and reoxidation of this by exposure to air. Some
of the processes for effecting this are tedious and deficient in accu-
racy, but the following, in one of which the reduction is effected
by a ferrous hydroxide and in the other by a hyposulphite, are
recommended by C. R a w s o n. The iron process is conducted by
treating 1 gramme of the finely powdered sample in a flask with
2 grammes of crystallized ferrous sulphate, 5 of caustic soda, and
1000 c.c. of water. The flask is closed by a cork having three
perforations, through one of which passes a syphon, while the
other two are used for the entrance and exit of a current of coal-
gas. The contents of the flask are maintained at a temperature a
little below the boiling point for $1\frac{1}{2}$ to 2 hours, when the source of
heat is removed and the insoluble matters allowed to subside.
A measure of 500 c.c. ($= \frac{1}{2}$ gramme of the sample) is now syphoned
off, and the reduced indigo oxidized by passing a current of air
through the solution. To complete the precipitation, the liquid is
acidified, and the precipitate of indigotin, mixed with indirubin
and indigo-brown, allowed to subside. The supernatant liquid is
passed through a weighed filter, and the precipitation washed
several times by decantation with hot water. It is then boiled
with alcohol, which dissolves the brown and red coloring matters,
allowed to cool to insure the separation of any traces of dissolved
indigotin, transferred to the filter, washed with rectified spirit, and
the pure indigotin dried at 100° and weighed.

The following method is preferred by C. R a w s o n, as leaving
nothing to be desired in point of accuracy, and being more rapid

than any other reduction-process:—1 gramme of the finely pow-
dered sample is made into a paste with water, and treated in a
flask with about 600 c.c. of lime-water. The flask is closed by a
cork having four perforations, two of which serve for the passage
of a current of coal-gas, a third carries a syphon, while to the
fourth is fitted a tap-funnel. The contents of the flask are heated
to 80° C., and 100 to 150 c.c. of a strong solution of sodium hypo-
sulphite ($NaHSO_2$) introduced through the tap-funnel.[1] In a few
minutes the liquid assumes a yellow tint, and is maintained at a
temperature near the boiling point for half an hour. After allow-
ing the insoluble matter to subside, an aliquot part of the solution
should be removed and a current of air drawn through it for about
twenty minutes, when it is acidulated with hydrochloric acid.
The precipitate, consisting of a mixture of indigotin and indirubin,
is collected on a weighed filter, thoroughly washed with hot water,
dried at 100°, and weighed. It is then exhausted by boiling
alcohol, whereby the indirubin is dissolved, and can be estimated
from the loss of weight or recovered by evaporating the alcoholic
solution.

Although, with care, the precipitate of mixed indigotin and
indirubin obtained as above may usually be obtained free from
impurities, in some cases Rawson recommends that the dried
precipitate should be dissolved in pure concentrated sulphuric
acid at 85° C., and an aliquot part of the diluted solution titrated
with $\frac{N}{50}$ permanganate, each 1 c.c of which, according to him, cor-
responds to 0.0015 gramme of indigotin.

In a method described by H. M. R a u (*Jour. Amer. Chem. Soc.*,
1885, 7, 16), which is a modification of one previously suggested
by F r i t s c h e (*Annal. Chem.*, xliv. 290), the indigo is reduced
in alkaline solution by glucose. The operation is conducted in a
weighed flask of about 8 oz. capacity, fitted with a cork carrying
two tubes. From $1\frac{1}{2}$ to 2 grammes of the sample of indigo, 3 to 4
of pure grape sugar, from 5 to 10 c.c. of a 40 per cent. solution of
caustic soda, 60 c.c. of water, and about 120 c.c. of rectified spirit

[1] The sodium hyposulphite, which must not be confounded with the thio-
sulphate, $Na_2S_2O_3$, is prepared by treating a solution of sodium hydrogen sulphite
($NaHSO_3$) with zinc-dust in a closed flask. After standing about one hour, with
occasional agitation, the liquid is decanted and diluted with a litre of recently
boiled distilled water. About 50 grammes of slaked lime should be next added,
the vessel closed, and when the precipitate has subsided the clear liquid is
syphoned off and kept under a layer of kerosene oil, in a bottle protected from
the light.

are employed, and the total weight of the apparatus is observed. The flask is heated in a water-bath for half an hour, and allowed rest for another hour. One of the two tubes is then connected with an apparatus generating carbon dioxide, by which the liquid is blown out through the other tube, which is arranged as a syphon, and the shorter limb of which is loosely plugged with glass-wool. The weight of the liquid expelled is noted, and the indigotin is then precipitated by passing a current of carbon dioxide for about fifteen minutes, and this is followed by a current of air to complete the precipitation. The precipitate is crystalline, and is readily washed. It is stated by Rau to represent the indigotin and indirubin of the sample, but Rawson has pointed out (*Jour. Soc. Dyers, &c.*, i. 211) that the solubility of indirubin in alcohol renders its precipitation improbable, and he has proved by actual experiment that the precipitate obtained by Rau's process consists of pure *indigotin*, yielding nothing either to cold alcohol or to ether.

A volumetric method of determining indigotin has been described by L. M. N o r t o n (*Amer. Assoc. Adv. Science*, 1880, p. 358). One gramme of the sample is mixed in a mortar with milk of lime, and the paste washed into a flask. One gramme of zinc-dust is added, and water added to a mark on the neck. The flask is then heated on the water-bath for half an hour, closed, and allowed to stand overnight. In the morning the contents are shaken, allowed to settle, and a volume of 100 c.c. blown out by a neutral gas into a solution of iron-alum. The ferrous salt formed corresponds to the reduced indigo in the volume taken, and is determined by titration with a standard solution of bichromate. H e l e n C o o l e y (*Amer. Jour. Anal. Chem.*, ii. 133) states that the manipulation is simple, and that, with some practice, the method gives good results.

A variety of methods of assaying indigo has been based on the oxidation of the coloring matter in acid solution. Thus, potassium permanganate, bichromate, and ferricyanide have all been recommended and used to a considerable extent, and bleaching powder solution has also been employed. All these processes are open to the objection that the oxidizing agent acts on the indigo-gluten and ferrous salts, as well as on the indigo-red and indigo-blue, and hence the results are liable to be seriously above the truth; but Rawson has pointed out that the errors due to this cause may be practically avoided by previously precipitating the sulphindigotic acid in the form of the sodium salt, by adding

common salt to the solution. He recommends the following method of working:—1 gramme of the sample of indigo in the form of impalpable powder is mixed in a small mortar with about its own weight of ground glass. This mixture is gradually and carefully added, during constant stirring with a glass rod, to 20 c.c. of concentrated sulphuric acid (sp. gr. 1.845), which is then heated to about 85° C. for an hour.[1] The product is then cooled, diluted with water to 1 litre, and filtered from indigo-brown and other insoluble matters. If the solution be now at once titrated with permanganate the results are liable to be seriously above the truth, owing to the presence of sulphurous acid, ferrous salts, indigogluten or the products of its decomposition, and other oxidizable matters.[2] To eliminate this source of error, Rawson recommends that 50 c.c. of the filtered solution should be treated with 50 c.c. of water and 32 grammes of common salt, which quantity is almost sufficient to saturate the liquid. After standing for two hours,[3] the solution is filtered and the precipitate washed with about 50 c.c. of brine of 1.2 sp. gr. The precipitated sodium sulphindigotate is dissolved in hot water, and the solution cooled, mixed with 1 c.c. of sulphuric acid, and diluted to 300 c.c. This solution is then titrated in a porcelain dish with a solution of potassium permanganate, containing 0.5 gramme of the solid salt per litre,[4] the exact oxidizing power of which has been ascertained by experiment with a solution of pure indigotin. This is made by dissolving 0.5 gramme in strong sulphuric acid, diluting the

[1] The temperature and time recommended in the test should not be greatly exceeded. The sulphuric acid employed for dissolving the indigo must be free from arsenic and nitrous compounds. The first condition may be ensured by well-known means, the second by heating the acid with a few crystals of ammonium sulphate. As sulphurous acid is liable to be formed during the sulphonation of the indigo at a high temperature, unless it is carefully removed a serious error may be introduced. To avoid this difficulty it is recommended to add to the sulphuric acid about 40 per cent. of its weight of phosphoric anhydride; no external heat is there necessary, and the sulphonation is completed in about two hours with a very slight rise in temperature.

[2] For this reason indigo is frequently adulterated with reducing agents such as oxalic acid.

[3] Rawson states that if the liquid be strongly agitated, by drawing a current of air through the solution, the precipitate completely separates in less than half an hour.

[4] Instead of permanganate of this strength, $\frac{N}{50}$ solution (0.6324 gramme per litre of $KMnO_4$) may be used. According to Rawson, 1 c.c. of this oxidizes 0.0015 gramme of indigotin.

solution to 1 litre, and employing 50 c.c. of the solution and 250 c.c. of water for the titration. The oxidation is regarded as complete when the liquid, which first takes a greenish tint, changes to a light yellow, with a faint pink color on the margin. A correction should be made for the small quantity of sodium sulphindigotate which escapes precipitation by the salt, and which Rawson finds to be equivalent to 1 milligramme of indigotin.

Instead of precipitating the sodium sulphindigotate by salt, as recommended by Rawson, it is in many cases sufficient to mix the sample of indigo with powdered glass, and treat with hot hydrochloric acid of moderate strength, filtering, washing the insoluble portion with a mixture of alcohol and ether, drying, and treating with sulphuric acid.[1] Whether or not this treatment be substituted for precipitation of the sulphindigotate, it is essential, in order to obtain accurate results, that the dilute solution in sulphuric acid should be *filtered*, to remove indigo-brown and other organic matters having a reducing action on the permanganate.

Other oxidizing agents, such as potassium ferricyanide or bichromate, which have been recommended for titrating the solution of sulphindigotate, present no advantage over permanganate, and the end-reaction is not so well defined.

Instead of assaying the solution of sulphindigotic acid or its sodium salt by an oxidizing agent, a suitable reducing agent may be substituted. M u l d e r has proposed the use of stannous chloride for the purpose, and B e r n t h s e n and D r e w s (*Chem. News*, xliii. 80) have suggested Schützenberger's hyposulphite of sodium ($NaHSO_2$) for reducing sulphindigotic acid. They find the reduction to occur in a strictly quantitative manner, according to the equation:—

$$C_{16}H_8N_2O_2(SO_3H)_2 + NaHSO_2 + H_2O = C_{16}H_{10}N_2O_2(SO_3H)_2 + NaHSO_3.$$
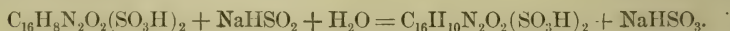
A. M ü l l e r has also recommended the utilization of this reaction, and C. R a w s o n considers that, of all the volumetric methods which have been devised for estimating "indigotin," the hyposulphite process is capable of giving the most rapid and accurate results, but considerable care and delicacy are required in the manipulation.

If iron be present in the ferric state, the results obtained by the

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[1] If the treatment with salt be omitted, the solution of the indigo in sulphuric acid should be somewhat diluted, boiled for fifteen minutes to drive off sulphurous acid, cooled, and diluted to 1 litre.

hyposulphite process will be above the truth, but it is only in the lower classes of indigo that this impurity is present, and in those cases it principally exists in, or becomes subsequently reduced to, the ferrous state. Of course, treatment of the sample with hydrochloric acid, or precipitation of the sulphindigotate by salt, can be resorted to if requisite. Neither indigo-gluten, indigo-brown, nor indigo-red has any appreciable oxidizing action on sodium hyposulphite. Hence the method is one which effects a determination of *actual indigotin* present, and is in that respect less adapted for the commercial valuation of indigo than a method like that of oxidation by permanganate, which also takes cognizance of the indirubin of the sample.

The use of sodium hyposulphite for reducing indigo in presence of an alkali has already been described. Its application to acid solutions of indigo and to the assay of indigo-carmine is carried out by Rawson as follows:—A standard solution of cupric sulphate is prepared by dissolving 1.904 gramme of the crystallized salt $(CuSO_4,5H_2O)$ in water, adding 100 c.c. of strong ammonia (sp. gr. 0.880), and diluting to 1 litre. 50 c.c. of this solution is boiled in a wide-mouthed flask of about 200 c.c. capacity, to expel air, and allowed to cool. The flask is fitted with a caoutchouc stopper pierced with four holes, two of which serve for the entrance and egress of a current of coal-gas, while into the other two are fitted the noses of two Mohr's burettes containing the solutions of sodium sulphindigotate and sodium hyposulphite respectively. The latter solution should be of one-fifth of the strength of that employed for the alkaline reduction-process, and the burette containing it is attached to the stock-bottle of standard solution in such a manner that it can be refilled without introducing air. A current of coal-gas (previously caused to traverse a U-tube, charged with a mixture of milk of lime and solution of ferrous sulphate) is passed through the flask containing the measured quantity of copper solution, and the solution of sodium hyposulphite is then gradually run in until the liquid becomes nearly colorless, when a few drops of indigo-carmine solution are added from the other burette, and finally a further quantity of hyposulphite is added until the solution assumes a peculiar brownish-red color. The volume of hyposulphite employed, after making a slight correction for that requisite to reduce the sulphindigotate, represents the quantity required to reduce .050 gramme of indigotin, this being the amount to which 50 c.c. of the standard copper solution is equiva-

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lent. The strength of the hyposulphite solution having been thus ascertained, a measure of 50 c.c. of sulphindigotic acid solution, prepared as already described, is introduced into the flask, boiled to expel the air, and allowed to cool. The flask is then attached to the burettes, coal-gas passed as before, and the hyposulphite solution gradually added during constant agitation. With pure indigotin and the better qualities of indigo, the liquid, when fully reduced, becomes of a pale yellow tint, but in the case of inferior samples it has a more or less dirty brownish-yellow color. In both cases, however, the end of the reaction is perfectly well defined.

C. Rawson (*Jour. Soc. Dyers, &c.*, i. 79) gives the following figures showing the results yielded by six typical samples of commercial indigo when examined by the principal of the methods already described.

	JAVA.	BENGAL.	BENGAL.	OUDE.	KURPAH.	MADRAS.
Water.	2.99	5.22	6.17	7.50	8.05	5.71
Ash.	1.99	3.91	4.86	8.21	25.72	33.62
Indigotin; by sublimation.	60.84	57.50	49.36	41.60	41.92	39.56
Indigotin; volumetric, by hyposulphite.	68.78	59.26	55.66	43.18	42.52	36.80
Indigotin; gravimetric, by $FeSO_4$ and NaHO.	68.24	58.84	54.34	44.50	41.50	34.50
Indigotin; gravimetric, by hyposulphite and lime.	68.97 }	59.12 }	56.20 }	43.42 }	42.68 }	35.21 }
Indirubin; separated by alcohol.	4.23 }	3.50 }	2.80 }	3.65 }	2.45 }	3.98 }
Indigotin and indirubin; titration with $KMnO_4$ direct.	76.18	66.71	62.66	50.04	47.15	39.50
Indigotin and indirubin; after precipitation with salt.	73.55	63.50	57.50	44.90	43.10	37.40

Helen Cooley (*Amer. Jour. Anal. Chem.*, ii. 137) gives the following figures (among others) in illustration of the results yielded by different processes of assaying indigo.

	KURPAH.		BENGAL.		OUDE.	GUATEMALA.
	Red.	Blue.	Red.	Blue.		
Indigotin; by sublimation.	45.40	56.34	55.99	57.54	62.58	47.03
Indigotin; gravimetric, by NaHO and glucose.	45.28	55.21	53.79	57.06	57.72	47.10
Indigotin; volumetric, Norton's process.	45.48	55.23	53.13	57.27	51.53	47.14
Indigotin and indirubin; precipitation with salt and titration with $KMnO_4$.	. .		64.10	60.89	51.88	. .

In criticising these results (*Amer. Jour. Anal. Chem.*, ii. 368), C. R a w s o n points out that higher figures are to be expected by a process which takes cognizance of the presence of indirubin than by one which is unaffected by this constituent of indigo, and he attributes the higher results obtained by the permanganate process at least in part to this cause, though over-heating with sulphuric acid may also have contributed to the result. In a sample of African indigo he has met with 8 per cent. of indirubin and 32 of indigotin.

The assay of indigo by dyeing swatches of cloth under specified conditions is useful in some cases, but the results cannot be compared in accuracy or delicacy with those obtained by chemical methods; and on assaying a series of samples a repetition of the test will very frequently fail to show the same graduation between them. The method of operating is to mix 2 grammes of the sample of indigo and 1 gramme of lime into a paste with water, transfer the mixture to a large beaker, add 1 gramme of zinc-dust, and make up the volume to 600 c.c. The whole is then heated on the water-bath for an hour, and a piece of white calico or swatch of cotton yarn of known weight introduced. It is then removed, squeezed, and exposed to the air till the blue color is fully developed, when it is compared with similar pieces of cotton which have been dyed by pure indigotin, or standard indigotin, in precisely the same manner.

A preferable method to the above is to treat 0.5 gramme of the sample with 6 grammes of strong sulphuric acid at 85° C. for an hour, and dilute the solution to 1000 c.c. 10 c.c. of this solution is then further diluted with a known quantity of water, and used for dyeing 5 grammes of white wool. About .05 gramme of sodium sulphate and a drop or two of sulphuric acid may be advantageously added to the bath before immersing the wool.

A colorimetric test, based on the depth of tint of the sulphindigotic solution, can be made under favorable conditions, but is valueless for comparing samples of indigo containing variable proportions of indigo-red and other secondary coloring matters, owing to the different shade which the solution possesses in such cases. C. H. W o l f f (*Jour. Soc. Chem. Ind.*, iii. 516) has proposed to avoid this difficulty by observing the absorption-spectrum of the solution (1 in 800,000). H. C o o l e y states that the method gives fair results with indigoes of high qualities, but is useless for the lower grades.

J. B r a n d t (*Rev. gen. des. Mat. Color.*, 1897, No. 2) gives a method for the estimation of indigo by extracting the commercial sample with aniline oil in a Soxhlet apparatus. On allowing the aniline to cool the pure indigo crystallizes out. Water and hydrochloric acid are added and the indigo filtered on a tared filter, washed with boiling water, and then with cold alcohol, dried, and weighed. A somewhat similar method is employed by S c h n e i d e r, only he uses naphthalene as a solvent instead of aniline.

G e e l a n d also proposes a similar method, using nitrobenzene as the solvent, while B r y l i n s k i uses glacial acetic acid.

F. A. O w e n (*Jour. Amer. Chem. Soc.*, xiii. 32) gives a method for determining indigotine for commercial purposes. A sample of the indigo is finely ground in a mortar with water, and the whole transferred to a 200 c.c. flask. 3 grammes of zinc-dust and 60 c.c. of ammonia (concentrated) are added, the flask then filled up with water to $\frac{1}{2}$ c.c. above the 200 c.c. mark and shaken. From half an hour to 2 hours is required for the reduction, during which period the shaking of the flask is continued at intervals. When the residue is complete the froth will subside and the solution will become pale yellow, or with some samples which contain chlorophyll or other non-reducible green coloring matter, greenish-yellow. 50 c.c. of the solution are then removed by a pipette from the flask to a beaker, or porcelain dish, 5 or 6 drops of ether added, and the whole agitated by blowing air through the pipette. The precipitated indigotine is acidified with hydrochloric acid, heated to boiling and collected on a tared filter-paper. Finally it is dried at 100° C. and weighed.[1]

G. E n g e l proposes a method based on the fact that indigo can be reduced quantitatively by a solution of vanadyl sulphate. The latter is prepared in the following manner: 10 grammes of ammonium vanadate are dissolved in 100 grammes of sulphuric acid of 66° B., with the aid of heat. The resultant red solution is poured into two litres of water of 50° C. To this are added by degrees 50 grammes of zinc powder until the solution shows a purplish-blue color. Filter and allow to cool.

The titration is performed in the presence of a current of carbon dioxide. The vanadyl sulphate solution is run from a burette into a measured solution of indigo carmine until the color of the latter has disappeared.

[1] The indigotine obtained in this way is not pure.

F. U l z e r recommends the following method for the commercial valuation of indigo: A solution of sodium stannite is prepared by the addition of sodium hydrate to 10 c.c. of a solution of stannous chloride containing 88 grammes of the crystallized salt per litre. About 0.8 gramme of finely powdered indigo is mixed with this solution, and allowed to stand with occasional agitation, for an hour, to effect the reduction of the indigotine. 15 c.c. of hydrogen dioxide solution (10 vols.) are added, and the whole allowed to stand for another hour; then the mixture is acidified with dilute sulphuric acid, heated to boiling and filtered through a tared filter. The precipitate after being washed successively with boiling water, dilute caustic potash, and hot alcohol, is dried at 100° C., and weighed. It is then ignited and the weight of the ash deducted from the previous weighing, the difference giving the amount of indigotine present. The treatment with dilute sulphonic acid removes from the indigo indigo-glutin and similar matters, that with potash and alcohol the indirubin (indigo-red), respectively.

The following results were obtained by this method:— .

SOURCE.	INDIGOTINE. Per Cent.			INDIRUBIN. Per Cent.	
	I.	II.	III.	I.	II.
Indigotine (prepared by Fritzsche's method).	99.64	. .	. .	. .	. .
Bengal indigo (medium quality).	70.10	70.01	69.45	2.29	. .
Benares indigo (native manufacture).	69.01	68.11	.	2.67	2.23
Indigo manufactured by ammonia process).	44.71	45.29	. .	1.49	1.73

DETECTION OF INDIGO ON THE FIBRE. The coloring-matter deposit in the fibre when a fabric has been dyed in the indigo-vat consists essentially of indigotine, but when soluble indigo has been employed the dye is taken up in the form of mono- or di-indigotin-sulphonic acid.

Fibres dyed in the indigo-vat are unaffected by hydrochloric acid, dilute sulphuric acid, soda, or ammonia. On heating with

an acid solution of stannous chloride the fibre becomes paler, and a greenish-yellow solution is formed. Concentrated sulphuric acid gives a blue solution, and boiling absolute alcohol also dissolves the dye with blue color, the solution becoming colorless on standing, with separation of indigotine. Chloroform, amylic alcohol, glacial acetic acid, phenol, and aniline also give blue solutions when heated with indigo-dyed fibres.[1] On carefully heating a fabric which has been dyed in the indigo-vat, it gives off purple vapors, which can be condensed on the cover of a porcelain crucible to a blue spot.

Indigo is now frequently used in admixture with other coloring matters, some of which are difficult to recognize in presence of indigo. W. Lenz (*Jour. Soc. Dyers, &c.*, iii. 127, 140, 150, 178) states that woolen goods (*e. g.*, yarn) which have been dyed with vat-indigo only satisfy the following conditions:—Water, even when hot, should not extract any coloring matter; alcohol, of 50 and 95 per cent. strength by volume, should not, as a rule, extract any coloring matter on *gently* warming; oxalic acid solution saturated cold, cold saturated borax solution, 10 per cent. alum solution, and solution of ammonium molybdate in two parts of water should none of them, when used boiling, extract any coloring matter from the fibre; and the borax solution should not be colored red by hydrochloric acid (campeachy), or give a blue coloration or precipitate on subsequently adding ferric chloride (prussian blue). On the other hand, the blue color should be completely destroyed on warming the fibre with an acid solution of stannous chloride or ferric chloride. Glacial acetic acid should entirely remove the color after repeated treatment, and on treating the solution obtained with twice its measure of ether, and adding water in sufficient quantity to cause the ether to separate, the ethereal layer should appear distinctly, but not very intensely, blue, while a deposit of indigotine should appear at the junction of the two layers. The lower layer should be colorless, and remain so when a little concentrated hydrochloric acid is poured into it

[1] Strong nitric acid gives a yellow spot on indigo-dyed goods. This reaction is employed as a rough practical test for the quality of indigo-dyed goods. The cloth is first spotted with hydrochloric acid, which will produce no change with indigo, but will change logwood dyes to red. The fabric is then spotted with nitric acid, which, if the cloth be of good quality and indigo-dyed, will produce a yellowish-red stain, surrounded by a bluish-green ring. An inferior sample gives a red stain and no definite ring.

through the ether. On boiling the fibre with concentrated hydro-chloric acid, no sulphuretted hydrogen should be evolved; and after continued boiling, till the fibres are decomposed, treatment of the solution with strong caustic soda in large excess, warming, and adding a few drops of chloroform, no odor of isonitril should be observable (aniline blues).

Fibres which have been dyed with sulphonated indigo (indigo-carmine, soluble indigo) give a greenish-blue solution when treated with hydrochloric acid, and strong sulphuric acid yields a blue solution. Little or no color is removed in alcohol. Caustic soda turns the fibre greenish, and on boiling with the dilute alkali the dye is removed without the solution becoming much colored, until it is acidulated, when it becomes blue. Ammonia behaves simi-larly. The color is also removed by boiling with dilute sodium carbonate, and silk or wool may be dyed blue in the acidulated solution. Heated with an acid solution of stannous chloride, the fibre is decolorized. With nitric acid, goods dyed with sulpho-nated indigo behave like those dyed in the indigo-vat. When boiled with a solution of borax (saturated in the cold), goods dyed with indigo-carmine are decolorized, while if dyed with vat-indigo the color is not affected. Indigo-carmine colors the borax solution blue, and the liquid is decolorized when warmed with stannous chloride and hydrochloric acid. Glacial acetic acid does not re-move the color from fibres dyed with indigo-carmine.

The determination of the amount of indigotin fixed on fibres is sometimes of interest, since, as a rule, neither the quantity of in-digo contained in the vat nor the exact quality of the indigo used is known. The determination may be effected by completely ex-tracting the fibre with glacial acetic acid, precipitating the indigotin from the resultant solution by addition of water, and either at once collecting and weighing it or determining it by one of the processes used for the assay of commercial indigo. In some cases it is de-sirable to remove other coloring matters from the fibre by treat-ment first with cold hydrochloric acid, and then with a boiling solution of oxalic acid saturated in the cold. Sulphonated indigo is not stripped by glacial acetic acid, but may be removed from the fibre by boiling with borax solution in the manner already described.

A. Renard (*Jour. Soc. Dyers, &c.*, iii. 4) determines the indigo on fabrics by a direct application of sodium hyposulphite and lime to the fibre. He treats 10 grammes of the fibre with 200 c.c. of a

solution prepared by adding 2 litres of water and 100 c.c. of milk of lime to 100 c.c. of neutral sodium hyposulphite prepared from bisulphite solution of 1.32 sp. gravity. The liquid is heated to 60° or 70° C. till the fibres are decolorized, when a current of coal-gas is passed through the flask employed and the contents shaken till every trace of blue has disappeared, when the liquid is decanted into a graduated cylinder without interrupting the current of gas. After cooling, the exact volume of the decanted liquid is observed, excess of hydrochloric acid added, and the precipitated indigotine filtered off after twelve hours, washed, dried, and dissolved in sulphuric acid, the resultant solution being subsequently titrated with standard hyposulphite, as described on p. 401. Renard found the amount of indigotine fixed on cotton fibre to range from 1 to 3 per cent. The method is applicable in presence of aniline blues, and with an obvious modification would serve for the assay of fabrics dyed with sulphonated indigo.

To distinguish indigo-blue from indoin-blue on the fibre, the material should be worked in a strongly alkaline bath of soap and soda; indigo-blue will remain unchanged, but indoin-blue becomes greyish. If the sample is passed several times through a bath of sulphuric acid at 1° Bé., rinsed, and dried, indigo-blue will show no change, but indoin-blue will acquire a reddish tone.

Coloring Matters from Lichens.

Several kinds of lichens acquire a violet color under the joint influence of ammonia and atmospheric oxygen. This fact depends on the presence of one or two peculiar principles, and was known and practically utilized long before it received a satisfactory explanation.

The coloring matters of industrial importance obtained from lichens are three in number, namely:—*Archil*, *orseille*, or *orchil*; *cudbear*, known on the Continent as *perseo*; and *litmus* or *tournesol*. The two principal species of lichen which yield archil are *Rocella fuciformis*, which furnishes the products from Lima, Angola, Zanzibar, Ceylon, and Mozambique; and *Rocella tinctoria*, growing in Cape Verde and the neighboring islands, Chili, &c. The first species contains a peculiar principle called e r y t h r i n, convertible into a red dye by the united action of air and ammonia; while the latter contains, in addition, a chromogen called l e c a n o r i c or o r c e l l i c a c i d and its homologue e v e r n i c a c i d. Cudbear is obtained from the Swedish lichen, *Lecanoria tartarea*.

The value of the various lichens or "archil weeds," from which archil and the allied coloring matters are prepared, depends on the proportion of orcin obtainable from them. This may be ascertained approximately by the following volumetric process devised by S t e n h o u s e :—10 grammes weight of the finely divided lichen is macerated three or four times in succession with a dilute solution (5 per cent.) of caustic soda, each treatment being only extended to.a few minutes' duration. The strained or filtered solutions are then mixed and titrated with a standard solution of sodium hypochlorite, which must be gradually added. Each drop of the hypochlorite produces a blood-red coloration, which changes to yellow in the course of a few seconds. The addition is continued cautiously as long as this reaction is produced. The hypochlorite solution must be freshly prepared, and its strength ascertained by titration with pure orcin or a lichen of known quality.

S. R e y m a n n has proposed to assay archil weeds for orcin by acidulating the solution obtained by macerating the lichens with caustic soda and titrating the solution with a hypobromite.

ERYTHRIN or ERYTHRIC ACID, $C_{20}H_{22}O_{10}$, may be prepared from *Rocella fuciformis* by macerating the lichen in the cold with milk of lime. The filtered liquid is acidulated with hydrochloric acid, when the erythrin is precipitated as a hydrate of the formula $2C_{20}H_{22}O_{10} + 3H_2O$, which is filtered off and washed. It becomes anhydrous at 100° and melts at 137° C. Erythrin in nearly insoluble in cold water, but dissolves in 240 parts of boiling water, and is deposited from the hot solution on cooling as a colorless crystalline powder, only slightly soluble in cold alcohol or ether, but more soluble in hot alcohol, from which solvent it crystallizes in stellate groups of needles. The solution gives a white precipitate with basic lead acetate, but none with the neutral acetate. With ferric chloride it gives a fine purple or violet coloration, changing to a brownish-red precipitate with excess of the reagent. Erythrin exhibits the characters of a weak acid, dissolving in solutions of caustic and carbonated alkalies and of the alkaline earths, from which solutions it is thrown down as a bulky white precipitate on addition of an acid. The ammoniacal solution of erythrin becomes red on exposure to the air.

If the solution of erythrin in alkali be boiled, decomposition ensues, the erythrin splitting up into p i c r o-e r y t h r i n, $C_{12}H_{16}O_7$, and o r c e l l i n i c a c i d, $C_8H_8O_4$, while on further treatment

the picro-erythrin is decomposed into o r c i n o l, $C_7H_8O_2$, e r y t h r o l, $C_4H_{10}O_4$, and c a r b o n d i o x i d e. These reactions establish the constitution or erythrin as the d i - o r c i n i l l i c e t h e r o f e r y t h r o l, and that of picro-erythrin as the m o n o - o r c e l l i n a t e of the same alcohol. The relationship of these and allied bodies is shown by the following formulæ: [1]—

Orcinol, ... $C_6H_2(CH_3)(OH)_2.H$

Orcellinic acid, . . . $C_6H_2(CH_3)(OH)_2.CO.OH$

Diorcellinic acid, . . $\begin{cases} O.C_6H_2(CH_3)(OH).CO.OH \\ CO.C_6H_2(CH_3)(OH)_2 \end{cases}$

Erythrin, ... $\begin{matrix} C_6H_2(CH_3)(OH)_2.CO.O \\ HO \\ HO \\ C_6H_2(CH_3)(OH)_2.CO.O \end{matrix} \left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} C_4H_6^{(iv)}$

Picro-erythrin . . . $\begin{matrix} C_6H_2(CH_3)(OH)_2.CO.O \\ HO \\ HO \\ HO \end{matrix} \left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} C_4H_6^{(iv)}$

Erythrol, ... $\begin{matrix} HO \\ HO \\ HO \\ HO \end{matrix} \left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} C_4H_6^{(iv)}$
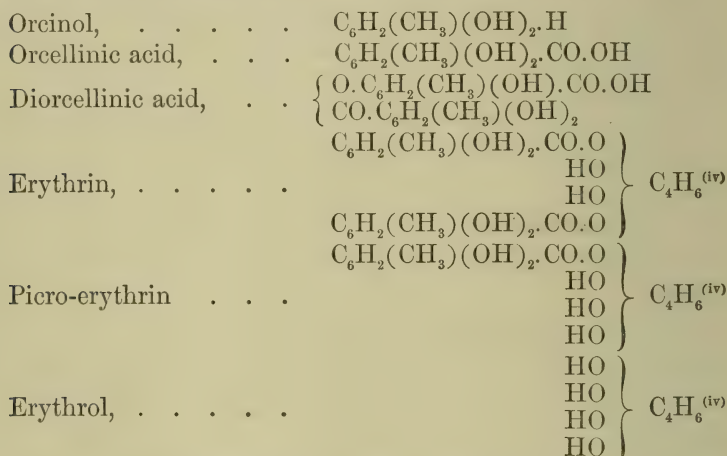
PICRO-ERYTHRIN, $C_{12}H_{16}O_7$, is only slightly soluble in cold water, but very readily in hot, and on cooling the solution is deposited in silky needles or shining plates, melting at 158° C., and having at once a slightly sweet and intensely bitter taste. With ammonia, ferric chloride, and basic and neutral lead acetate it reacts like erythrin. Its behavior when boiled with alkalies has already been described.

LECANORIC, ORSELLIC, or DIORSELLINIC ACID. $C_{16}H_{14}O_7$. This substance bears the same relation to orcellinic acid that tannic acid (digallic acid) bears to gallic acid. It may be obtained by extracting the lichen *Rocella tinctoria* with ether, evaporating the solution, treating the residue with milk of lime, again filtering, precipitating the filtrate with sulphuric acid, and crystallizing the precipitated orcellic acid from alcohol. It is scarcely soluble in

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[1] Homologues of these bodies are obtainable from certain lichens. Thus h o m o e r y t h r i n, $C_{21}H_{24}O_{10}$, has been found in a stunted specimen of *Rocellia fuciformis*. E v e r n i c a c i d, $C_{17}H_{16}O_7$, occuring in *Evernia Prunastri;* and u s n i c a c i d, $C_{18}H_{18}O_7$, and b a r b a t i c a c i d, $C_{19}H_{20}O_7$, found in *Usnea barbata*, are homologous with orsellic acid, and split up in a similar manner when boiled with alkalies.

cold water, and requires 2500 parts of boiling water for solution, but dissolves more readily in alcohol and ether.   It forms prismatic needles containing 1 *aqua*, which become anhydrous at 100°, and melt at 153° C. with decomposition and evolution of carbon dioxide.   The alcoholic solution of lecanoric acid gives no precipitate with lead acetate, but yields with cupric acetate a pale green precipitate after standing.   Ferric chloride produces a dark purple-red color, and ammonio-nitrate of silver is reduced on heating. When boiled with water, lecanoric acid undergoes hydrolysis, and is converted into o r c e l l i n i c   a c i d, $C_8H_8O_4$.   Boiled with alcohol it yields e t h y l   o r c e l l i n a t e (pseudo-erythrin).

ORCELLINIC ACID.   Dihydroxytoluic Acid. $C_6H_2(CH_3)(OH)_2$. COOH. [COOH:OH:CH_3:OH_2 = 1:2:4:5].   This substance results from the hydrolysis of lecanoric acid (see above), but is best prepared by heating erythrin on the water-bath with baryta-water, until barium carbonate begins to separate.   When a sample no longer gives a gelatinous precipitate on adding hydrochloric acid, the liquid is acidulated, when orcellinic acid gradually precipitates. It can be crystallized from acetic acid or dilute alcohol in stellate masses, which contain 1 *aqua*, become anhydrous at 100°, and melt with partial decomposition at 176° C.   Orcellinic acid is readily soluble in water, the solution gradually decomposing into o r c i n o l and carbon dioxide when boiled alone or with alkalies. It is colored a purple-violet by ferric chloride, and yields an amorphous precipitate with ammoniacal acetate of lead.

Orcellinic acid is characterized by the great facility with which it forms ethers.   Thus a m y l   o r c e l l i n a t e is readily formed by boiling erythrin (erythryl orcellinate) with amyl alcohol, and e t h y l   o r c e l l i n a t e, $C_8H_7O_4(C_2H_5)$, formerly called p s e u d o-e r y t h r i n, is always obtained when lichens containing erythrin are extracted with boiling alcohol.   It is slightly soluble in cold water, more readily in hot water or alcohol, and crystallizes in small needles or plates, which melt at 132°.   The aqueous solution is precipitated by lead acetate.

ERYTHROL, ERYTHRITE, or ERYTHROGLUCIN. $C_4H_6(OH)_4$.   This substance, which has the constitution of a tetratomic alcohol, is a product of the decomposition of picro-erythrin by alkalies, and exists ready formed in the *Protococcus vulgaris*.   It crystallizes in colorless dimetric prisms, fusing at 120° C.   It is readily soluble in water, sparingly in alcohol, and insoluble in ether.   Erythrol has a slightly sweet taste, is optically inactive, and does not reduce

Fehling's solution. When distilled with excess of strong hydriodic acid, it yields b u t y l   i o d i d e, C_4H_9I. By treatment with a mixture of strong nitric and sulphuric acid, it is converted into t e t r a n i t r o - e r y t h r o l, $C_4H_6O_4(NO_2)_4$, a body having marked explosive properties. By prolonged treatment with nitric acid, erythrol is converted into oxalic acid, no mucic acid being simultaneously formed.

ORCINOL.   ORCIN.   Dihydroxy-methylbenzene. $C_6H_3(CH_3)(OH)_2$.[m] This substance, which is homologous with resorcinol, and has the characters of a diatomic phenol, occurs in a free state in various species of lichens, and is a decomposition-product of the various acids and ethers contained in or prepared from these plants. It is best prepared by boiling erythrin (prepared as described on page 409) for half an hour with a slight excess of milk of lime, in an apparatus furnished with an inverted condenser, filtering, passing carbon dioxide through the filtrate, and evaporating the solution nearly to dryness. On agitating the concentrated liquid with hot benzene the orcinol is taken up, and can be obtained by separating and evaporating the solvent, while the erythrol remains in the aqueous layer. Orcinol may also be obtained by synthetical means.

Orcinol forms six-sided monoclinic prisms, melting at 58°, and containing $C_7H_8O_2 + H_2O$. The crystals effloresce gradually over sulphuric acid, and more rapidly when heated to 100°. The anhydrous substance melts at about 107°, and dilutes with some decomposition at about 287° under atmospheric pressure, but may be obtained pure and colorless by distillation *in vacuo*. When pure, orcin is colorless, but it acquires a pale reddish-brown color on exposure to air. It has an intensely sweet, but unpleasant, astringent taste. Orcinol is extremely soluble in hot water, but much less so in cold. It is almost completely precipitated in fine needles when its concentrated solution is warmed with saturated brine. Orcin dissolves readily in alcohol and ether, but less easily in hot benzene. The crystals deposited from the ethereal solution are anhydrous. It is neutral in reaction, but possesses marked acid properties. It readily decomposes sodium carbonate, and precipitates silica from silicates.

With oxidizing agents orcinol yields oxalic acid. With concentrated sulphuric acid it gives a sulphonic acid. When treated with a solution of bleaching powder, orcin yields an intense purple-red coloration, which rapidly changes to yellow. The most minute trace of orcin may be detected by this reaction.

When an aqueous solution of orcin is mixed with ammonia and exposed to the air it acquires a deep purple color, owing to the formation of a body called o r c e ï n, identical with the coloring matter of *archil*. If carbonate of sodium or potassium be also present, a blue coloring matter is formed which is identical with that contained in litmus.

If an alkaline solution of orcinol be heated with a little chloroform, it becomes first purple-red and then bright red, and on dilution with water exhibits an intense greenish-yellow fluorescence, from the formation or homofluorescein, $C_{23}H_{18}O_5$. This reaction, first observed by S c h w a r t z (*Berichte*, xiii. 543), is so delicate that the compounds which yield orcinol on treatment with alkalies can readily be detected by this means in the lichens containing them, by simply boiling a few pieces of the plant with a 5 per cent. solution of caustic potash, adding a little chloroform to the clear liquid, then warming the solution for ten minutes more, and diluting it with water.

An aqueous solution of orcinol is not precipitated by mercuric chloride, lead acetate, cupric sulphate, tannin, or gelatin. With basic acetate of lead it yields a white precipitate, and with ferric chloride a violet-black coloration or red precipitate.

On addition of bromine-water to orcinol in aqueous solution, t r i b r o m o r c i n o l, $C_7H_5Br_3O_2$, is formed, and the reaction has been recommended by R e y m a n n for the quantitative determination of orcin and the assay of archil weeds. The process is carried out exactly like the volumetric determination of phenol by bromination.

ORCEÏN is the product of the action of ammonia and oxygen on orcinol. L i e b e r m a n n states that two compounds may be thus formed, containing respectively $C_{14}H_{11}NO_3$ and $C_{14}H_{12}N_2O_3$. The latter substance is the chief product when the ammonia is in excess, and is less soluble in alcohol and ammonia than the former compound. Both bodies form brown amorphous masses, having a beetle-green lustre. Orceïn is somewhat soluble in water with red color, but is reprecipitated from its solution by neutral salts of the alkali-metals. In ether it is insoluble, but dissolves readily in alcohol, yielding a scarlet solution. In fixed alkalies and ammonia orceïn dissolves with formation of splendid purplish-violet solutions.

Archil, ORCHIL, or ORSEILLE is the commercial coloring matter from *Rocella tinctoria* and *R. fuciformis*. It is usually prepared

by treating the finely chopped lichens with dilute ammonia, and keeping the mixture at about 20° C. till a dark violet paste has been formed. This when diluted with ammonia and filtered through a press yields *blue archil*, while on gently heating this till the ammonia is removed *red archil* is obtained. *French purple* is a lake obtained by precipitating the ammoniacal liquid obtained as above with calcium chloride. In using it, the coloring matter is treated with oxalic acid and boiled with water. The filtered liquid, when rendered slightly ammoniacal, dyes silk and wool a fine purple color.

Archil has lost much of its importance since the introduction of the coal-tar dyes, and is now chiefly used in combination with other coloring matters to obtain certain shades of brown, and for the production of a cheap blue on wool, the material being first lightly grounded with indigo and then passed through a bath of archil, when it is dyed a rich purple hue, similar to that produced by indigo alone.

Archil occurs in commerce in two forms, paste and liquor. The solid matter consists essentially of the impure orceïn in combination with ammonia. Archil varies greatly in quality, owing to differences in the weed employed, the care used in the manufacture, and the presence or absence of impurities. In some cases it contains an immoderate excess of ammonia, and in others the proportion of solid matter is abnormally low. This can be readily ascertained by drying a known weight of the sample at 100°. Occasionally the solid matter in archil paste is as low as 20 per cent. Spent weeds, from the manufacture of archil liquor, are sometimes added to the paste.

Archil liquors range in specific gravity from 1.040 to 1.080, or even to 1.100, but the density is no accurate indication of the dyeing power, which is best ascertained by a practical dyeing test on wool.

Archil paste is sometimes adulterated with other vegetable coloring matters. To detect these, J. W. Slater recommends that 3 or 4 grammes of the sample should be treated with 100 c.c. of water, and 50 drops of a solution of stannous chloride in twice its weight of water added. On boiling the liquid, a yellowish color only will remain if the archil be pure, but 3 to 4 per cent. of logwood liquor will yield a greyish-blue, and the color will be reddish if peach-wood, sapan-wood, or other red wood has been added as an adulterant.

Archil is decolorized by reducing agents, but the color returns on exposing the reduced liquid to the air. Its other reactions and the methods of detecting it will be gathered from the description of the methods of detecting it in wine (see previous volume), and from the following processes of examining the commercial substance for adulterants.

Archil is now frequently adulterated with aniline dyes, especially magenta, acid magenta, and methyl violet.

H. Crossley (*Jour. Soc. Dyers, &c.*, ii., 23) determines basic magenta in archil by diluting the sample, if necessary, with hot water, filtering, and evaporating the filtrate to dryness at 100°.[1]

The residue is reduced to powder, and a weighed portion is digested with strong ammonia, which dissolves the orceïn and leaves the magenta base. The solution is filtered, and the residue is washed with ammonia till no more coloring matter is removed, when it is dried at 100° and weighed. It should be proved to be magenta by dissolving it in dilute acetic acid and applying the ordinary tests (page 278). Another method for the detection of magenta consists in treating the residue obtained by evaporating the filtered solution of the sample on filter-paper with two or three drops of benzoic aldehyde or aniline oil, when the magenta will dissolve and color the paper crimson. A faint pink tint is obtained with pure archil after a few minutes, but this is not readily mistaken for the immediate and strong coloration given by magenta.

For the detection of magenta or methyl-violet in proportions greater than 1 per cent., E. Knecht (*Jour. Soc. Dyers, &c.*, ii., 58) employs cotton yarn dyed with chrysamine. This does not take up the coloring matter of archil, but is dyed red by magenta, and brownish-red by methyl-violet. For the determination of magenta in archil, Knecht evaporates the filtered liquid to dryness, extracts the residue with alcohol, filters, and evaporates the filtrate. This second residue is heated for about a minute with caustic soda, and the insoluble portion allowed to settle. After standing a few minutes the liquid is decanted, and the residue treated with a more dilute soda solution; the process is repeated as long as the liquid takes up coloring matter. The residue is then washed with water and weighed. On subsequently treating it with hydrochloric acid, it will dissolve with magenta or violet color, according to its origin. Safranine and the azo-dyes cannot be detected in this manner.

[1] T. Fairley (*Jour. Soc. Chem. Ind.*, v. 286) treats archil paste at once with strong ammonia, repeating the process till all the orceïn is removed.

Liebmann and Studer (*Jour. Soc. Chem. Ind.*, v. 287) test archil for magenta by saturating the largely diluted solution with sulphurous acid, when most of the orceïn is precipitated. On adding acetone to the filtered solution, genuine archil does not show any change of color, but if either basic or sulphonated magenta be present the liquid changes in a few minutes to violet. One-tenth per cent. of magenta in archil gives a strong coloration. If the liquid which was saturated with sulphurous acid be boiled, filtered, and a piece of cotton, mordanted with tannin and tartar-emetic, immersed in the filtrate, only magenta will be fixed on the fibre, and whether it be the acid or basic kind can be ascertained as described on page 278.

C. Rawson (*Chem. News*, lvii. 165) objects to the foregoing methods on the ground of want of delicacy, and recommends that an amount of archil paste or liquor containing 1 or 2 grammes of solid matter should be boiled with 50 c.c. of alcohol, and the solution diluted with 100 c.c. of water. From 15 to 20 c.c. measure of a solution of basic acetate of lead, of 1.25 sp. gr., is next added, and this is followed after stirring by a similar quantity of strong ammonia. With pure archil, the filtered liquid will be quite colorless, but if magenta be present it may either be color-less or pink, according to the amount of ammonia present in the solution; but in either case, on acidulating the liquid the charac-teristic color of magenta will be at once developed, no change occurring with pure archil. By a colorimetric test, using for com-parison an aqueous solution of magenta containing 0.001 gramme per 100 c.c. and acidulated with acetic acid, the proportion of magenta present may be determined, but in this case the lead pre-cipitate must be washed with a mixture of 5 parts of alcohol, 10 of water, and 1 of strong ammonia.

The foregoing test also serves for the detection of safranine and methyl-violet. On adding acetic acid to the ammoniacal filtrate, the liquid becomes bluish-violet, if the latter dye be present. Strong ammonia decolorizes methyl-violet and magenta, but scarcely affects the color of a solution of safranine, while strong hydrochloric acid changes the latter to blue, and turns solutions of magenta and methyl-violet yellow.

F. Breinl has pointed out (*Jour. Soc. Dyers, &c.*, iv. 46) that various azo-dyes, producing colors ranging from crimson to claret-red, are now in the market, under such names as orchil extract, orchil-red, orselline, &c., being intended as actual substitutes for

archil and cudbear, and, being cheaper than magenta, are more likely to be used for the adulteration of those coloring matters. Breinl gives a very complete list of such coal-tar colors, and a table of reactions by which they may be recognized.   He divides them into three groups, according to their behavior with common salt, and with basic acetate of lead (sp. gr. 1.25) in presence of 25 per cent. of alcohol.   Thus, on saturating the aqueous solution of the sample with common salt, the following coal-tar dyes are completely precipitated : Orsellin BB and orchil red B (Bayer & Co.), orchil red A (Bad. Anilin und Soda F.), cloth reds B and G (Oehler), Bordeaux G, BX, and Extra (Bayer), Bordeaux B (Actien Ges. für Anilin Fab.), fast reds A and B (Bad. Anilin und S. F.).   The following colors are almost completely salted out by similar treatment:—Azorubin S and orchil red G (Actien Ges. für Anilin Fab.), amaranth, carmoisin B (Bayer), magenta, basic coloring matters from magenta residues, and safranine.   On the other hand, acid magenta and other acid coloring matters from magenta-residues, orselline R and B (Höchst Color-works), and red-violet NRS. (Bad. Anil. und S. F.) are not precipitated by common salt.   A filtered extract of archil gives a slight precipitate with salt, which redissolves when washed with brine.   The coal-tar dyes which are not completely or partially precipitated by saturating their solutions with common salt may be distinguished from archil by boiling with a solution made by dissolving 10 grammes of crystallized stannous chloride in a mixture of 25 c.c. of concentrated hydrochloric acid and 50 c.c. of water.   When thus treated, a filtered solution of orchil or cudbear is decolorized or turned light brown; while acid magenta, acid coloring matters from magenta-residues, and red-violet NRS, acquire a darker and more bluish coloration, and orselline R and B an intense bluish-violet coloration.   These coloring matters again are only partially precipitated when a solution containing 25 per cent. by measure of absolute alcohol is treated with basic lead acetate; whereas archil is completely precipitated under these conditions, and the other coal-tar dyes already mentioned are not precipitated at all. By these reactions it is always possible to establish the presence of a coal-tar dye, even if it be not possible to identify it with certainty.

An admixture of brazil-wood, barwood, or logwood with orchil or cudbear may be detected by immersing cotton, mordanted with iron or aluminium, in the hot dilute solution of the suspected

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sample.[1] After half an hour's treatment the cloth is removed, and washed with warm soap solution. The orchil or cudbear will produce at most a faint pink color on the mordanted cotton, and this will be removed by boiling the cotton for a few minutes with alcohol, while if logwood be present, cotton mordants with iron will be dyed bluish-gray or black, and if mordanted with alumina salts bluish-violet. Brazil-wood will dye the iron mordant blackish-brown, and the alumina mordant red.

Cudbear, called on the Continent *Perseo*, is obtained by the action of ammonia or urine on various kinds of lichens, especially *Lecanoria tinctoria* and *Variolaria orcina*, and hence in its origin and properties is very similar to archil, from which it differs mainly in being free from all excess of ammonia and moisture, and in being reduced to a fine powder. It often contains a considerable proportion of mineral matter, usually common salt, which is sometimes added as an adulterant, but in other cases to reduce an unusually rich article to a uniform standard of quality. Genuine cudbear leaves from 5 to 12 per cent. of ash. Cudbear is liable to much the same organic sophistications as archil, and if it be boiled with water the filtered solution may be examined by the same methods.

C. R a w s o n (*Jour. Soc. Dyers*, &c., iv. 69) detects azo-dyes in cudbear by sprinkling a little of the sample on some concentrated sulphuric acid, when the formation of a streak of characteristic colors—green, blue, violet, etc.—often affords valuable assistance. To obtain further evidence of the presence of azo-coloring matters, he recommends that 5 to 10 grammes of worsted yarn should be dyed for an hour with about 10 per cent. of its weight in cudbear in a bath rendered faintly alkaline with ammonia. A fresh quantity of yarn is similarly dyed in the partially exhausted bath, whereby the greater part of the orceïn is removed from the solution. Sulphuric acid, equal to 3 per cent. of the weight of the yarn, is now added, and a third quantity of worsted yarn introduced. The azo-red is now deposited on the wool in a form sufficiently pure to allow of its subsequent identification. It is desirable, though not directly necessary, to treat a genuine sample of cudbear side by side with the sample.

Litmus, or *tournesol*, is prepared from various species of *Rocella*,

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[1] As the coloring matter of barwood is not readily extracted by water, it is best to boil 2 grammes of the suspected cudbear for 10 minutes with 50 c.c. of alcohol, and then dilute the solution with water to 200 c.c.

Variolaria, and *Lecanoria* by allowing them to ferment in presence of ammonia, as in the manufacture of archil, except that in the case of litmus potassium carbonate is likewise added. When the mass has become violet, stale urine, lime, and potash are added, and the mass is again allowed to ferment until it assumes a blue color, when it is mixed with chalk or gypsum and a little indigo, and made up into small tablets.

On extracting litmus with cold alcohol, a red coloring matter is obtained, which is unaffected by acids, and yields l i t m u s - b l u e and another substance on treatment with water. On evaporating this solution, and treating the residue with absolute alcohol and a little acetic acid, a scarlet coloring matter is removed, which is changed to purple by ammonia, while the pure litmus-blue remains behind as a brown powder, soluble in water to a reddish-brown solution, which is turned blue by the slightest trace of an alkali.

Azolitmin, $C_7H_7NO_4$, the characteristic coloring matter of litmus, may be obtained in a state of purity, according to D e L u y n e s, by digesting 1 part of orcinol with 1 of strong ammonia, 25 of crystallized sodium carbonate, and 5 of water, at 60°–80° C. for four or five days in a closed vessel. A blue liquid is thus obtained, which is diluted with water and slightly acidulated with hydrochloric acid, when a precipitate is formed, which, after being washed and dried, is regarded as pure azolitmin.[1] So obtained, azolitmin is a reddish-brown powder, but slightly soluble in water and insoluble in alcohol and ether. Azolitmin appears to have the characters of a weak acid, the salts of which are blue, and the potassium compound of which exists in litmus.

Litmus exhibits a very characteristic absorption-spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. On adding a drop of ammonia to the ethereal solution the liquid becomes blue, and an absorption-band is formed, which commences at *d*, where it is extremely black, and

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[1] K a n e prepares azolitmin by exhausting powdered litmus with water, mixing with clean fine sand and evaporating on a water-bath. Sufficient hydrochloric acid is added to give a red solution after the carbon dioxide has been driven off, and the evaporation is continued to dryness. The residue is washed with water and again evaporated on a water-bath, after which the sand is freed from its coating of pure azolitmin by treatment with weak ammonia, and the azolitmin is finally obtained from its solution by precipitation with sulphuric acid.

gradually diminishes to E.   On shaking the ethereal solution with
ammoniacal water, the coloring matter passes into the aqueous
liquid, and the blue solution shows a well-marked absorption-band
at D.   Addition of acid now changes the color to red, and the
band at D disappears, the spectrum of the acidified liquid resemb-
ling that of œ n o l i n, the coloring matter of red wine.

Litmus is not employed in dyeing or calico-printing, but is used
for coloring wine and vinegar, and in the laboratory is well known
as an indicator of neutrality.   Its indications are fairly delicate;
but the habit of regarding litmus as an infallible guide to neutrality
has seriously retarded progress in several directions.[1]   Of late years
this fact has been more generally recognized, and a number of
other indicators have been proposed.   Of these, two—namely,
helianthin or *methyl-orange* (page 158) and *phenolphthaleïn* (page
313)—deserve the fullest confidence, and one or other of them can
be employed advantageously in place of litmus in a large number
of cases.

In the following table, by R. T. T h o m s o n (*Journ. Soc. Chem.
Ind.*, vi. 198), is given an epitome of the indications yielded by
litmus, as compared with those given by phenolphthaleïn and
methyl-orange (which last is affected by strong acids only).   The
figures represent the number of atoms of hydrogen displaced by
sodium or potassium in the form of caustic alkali, when a com-
pound is formed having a neutral reaction to the indicator in
question.   Thus, when methyl-orange is used in the titration of
sulphurous acid the neutral point is reached when the alkali has
been added in quantity sufficient to form the compound $NaHSO_3$;
but when phenolphthaleïn is used the point of neutrality corres-
ponds to the formation of the salt Na_2SO_3.   By a combined use of
the two indicators valuable volumetric determinations can be
effected.   In employing phenolphthaleïn as an indicator, it must
be remembered that the results are vitiated by the presence of am-
monium salts.   In other cases, when a blank space appears in the
table, it is meant that the end-reaction is obscure, and not to be
depended on.

The table shows the basicity of acids with different indicators,
when titrated in aqueous solution with fixed caustic alkali.

[1] Litmus is still employed for the titration of lime and lemon juice, a purpose
for which, in the opinion of the author, it is very ill-suited, especially if sodium
carbonate be used for the neutralization (see *Analyst*, xiv. 25, 80).

Acids.		Methyl Orange.	Phenolphthalein.		Litmus.	
Name.	Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.
Sulphuric	H_2SO_4	2	2	2	2	2
Hydrochloric	HCl	1	1	1	1	1
Nitric	HNO_3	1	1	1	1	1
Thiosulphuric	$H_2S_2O_3$	2	2	2	2	2
Carbonic	H_2CO_3	0	{ 1 dilute }	0	. .	0
Sulphurous	H_2SO_3	1	2	. .	. .	. .
Hydrosulphuric	H_2S	0	{ 1 dilute }	0	. .	0
Phosphoric	H_3PO_4	1	2	. .	. .	. .
Arsenic	H_3AsO_4	1	2	. .	. .	. .
Arsenious	H_3AsO_3	0	. .	. .	0	0
Nitrous	HNO_2	{ indicator destroyed }	1	. .	1	. .
Silicic	H_4SiO_4	0	. .	. .	0	0
Boric	H_3BO_3	0	. .	. .	. .	. .
Chromic	H_2CrO_4	1	2	2	. .	. .
Oxalic	$H_2C_2O_4$	. .	2	2	2	2
Acetic	$HC_2H_3O_2$	. .	1	. .	{ 1 nearly }	. .
Butyric	$HC_4H_7O_2$	. .	1	. .	{ 1 nearly }	. .
Succinic	$H_2C_4H_4O_4$	. .	2	. .	{ 2 nearly }	. .
Lactic	$HC_3H_5O_3$	. .	1	. .	1	. .
Tartaric	$H_2C_4H_4O_6$	. .	2	. .	2	. .
Citric	$H_3C_6H_5O_7$	. .	3	. .	. .	. .

It will be seen that all indicators behave alike on titrating strong mineral acids with fixed caustic alkali ; in the titration of a weak acid with a strong base they differ, methyl-orange being most sensitive to alkalies and phenolphthaleïn to acids, while litmus occupies an intermediate place. Speaking generally, l a c m o i d (page 419), d i m e t h y l a m i d o - a z o b e n z e n e (page 147), c o c h i n e a l, and c o n g o-r e d (page 222) behave like methyl-orange, while t u r m e r i c behaves like phenolphthalein.[1] P h e n-a c e t o l i n and r o s o l i c a c i d (page 310) usually react like litmus, except that in the latter case a sharp neutrality-point is obtained in titrating sulphurous acid when the salt Na_2SO_3 is obtained.

Litmus gives a deep blue color with alkalies and a red with acids; alkaline carbonates also produce a blue color. As litmus is sensitive to carbonic acid and hydrogen sulphide (hydrosulphuric acid), when carbonates or sulphides are titrated in its presence, the carbonic acid and hydrogen sulphide gases which are liberated

[1] Thus saliva and milk are neutral to litmus paper, strongly alkaline to lacmoïd or congo-red. and acid to turmeric paper. Litmus is also useful for estimating the acidity of urine.

must be driven off by boiling before the end reaction is taken. Litmus is a good indicator for titrating the acids present in the normal salts of such alkaloids as quinine, strychnine, morphine, narceine, and papaverine, since these are neutral to litmus. The alkaloids of caffeine, narcotine, and thiobromine are also neutral to litmus, but their salts act like a corresponding amount of the free acid. Aniline, toluidine and quinoline, exhibit a neutral reaction toward litmus, and hence cannot be titrated by it.[1]

Red Dyes from Woods, &c.

A number of red coloring matters of vegetable origin are, or have been, used in dyeing. Thus, *madder* is the root of *Rubia tinctorum*, a herbaceous plant. Its cultivation is almost obsolete,

COMMERCIAL NAME.	BOTANICAL ORIGIN.	GEOGRAPHICAL ORIGIN.	COLORING PRINCIPLE.	
			Name.	Formula.
Madder.	Root of *Rubia tinctorum*.	Turkey, France, Holland.	Alizarin. Purpurin.	$C_{14}H_8O_4$ $C_{14}H_8O_5$
Logwood or Campeachy wood.	Wood of *Hæmatoxylon campechianum*.	West Indies, Mexico, South America.	Hæmatoxylin. Hæmatein.	$C_{16}H_{14}O_6$ $C_{16}H_{12}O_6$
Brazil wood; Pernambuco wood.	Wood of *Cæsalpinia Brasiliensis* and *C. Crista*.	Brazil, Pernambuco, Jamaica.	Brazilin.	$C_6H_{14}O_5$
Peach wood.	Wood of *Cæsalpinia echinata*.	Nicaragua, Sierra Nevada.	Brazilin.	$C_6H_{14}O_5$
Sapan wood.	Wood of *Cæsalpinia sapan*.	Siam, Japan, East Indies, &c.	Brazilin.	$C_6H_{14}O_5$
Sandal, Santal, or Sanders wood.	Wood of *Pterocarpus santalinus*.	East Indies, Ceylon, Madagascar.	Santalin.	$C_{15}H_{14}O_5(?).$
Barwood.	Wood of *Baphia nitida*.	Sierra Leone.	Santalin.	$C_{15}H_{14}O_5(?).$
Camwood, or Kambe wood.	Wood of species of *Pterocarpus*.	West coast of Africa.	Santalin.	$C_{15}H_{14}O_5(?).$
Alkanet.	Root of *Anchusa tinctoria*.	Levant, South Germany.	Alkannin.	$C_{15}H_{12}O_4$, or $C_{15}H_{14}O_4.$
Safflower.	Flowers of *Carthamus tinctoria*.	Southern Europe, South America, East Indies.	Carthamin.	$C_{14}H_{16}O_7.$

[1] In using litmus for titrations at night, a sodium flame should be employed; in this light the red color will appear perfectly colorless, while the blue will appear black.

and its characters have already been sufficiently described.   Other red coloring matters, as *logwood* and *brazil-wood*, are obtained from the wood of trees of considerable size; while *alkanet* is obtained from the cortical parts of a root, and *safflower* from the flowers of a kind of thistle.   The preceding table shows the origin of the more important red coloring matters derived from plants.

Logwood or CAMPEACHY is the most important of the red dye-woods,[1] and is imported in the shape of irregular blocks, having an average weight of about 400 pounds.   The coloring matter probably exists in the form of a glucoside, for when the trees are freshly felled the wood is colorless.   By the time the logs arrive in this country they have acquired a dark brownish-red color externally, while the inside is still pale yellow or light red.   The logs are reduced to chips or raspings, which are moistened with water and allowed to ferment, whereby the glucoside is converted into h æ m a t o x y l i n, and this is partially converted into h æ m a t e ï n by the action of the air.   The product is lixiviated with water, and the solution concentrated to obtain a *logwood extract*.   To obtain a good extract, the powder must not be too highly oxidized, and the concentration of the solution must be conducted at a temperature not exceeding 60° C., or the hæmateïn will be converted into a dark purple resinous matter which injuriously affects the brilliancy of the color.   An inferior extract is largely made from campeachy *roots*.

Logwood yields very little soluble and coloring matter to cold water, but from 14 to 18 per cent. of its weight to boiling water.[2]

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[1] For convenience of classification, logwood is here classed as a red dye-wood. Although the coloring matter of logwood is itself red, it is not used in practice to produce red shades, but rather violet, blue, and black.

[2] The following exhibits the relative proportions of extract in woods from different sources:—

NAME AND MARK OF WOODS.	PERCENTAGE OF WATER.	PERCENTAGE OF ASHES.	PERCENTAGE OF YIELD OF EXTRACT.	PERCENTAGE OF COMBUSTIBLE MATTER.
Yucatan logwood	13.00	1.09	20.20	65.71
Laguna logwood	12.38	0.96	21.00	65.66
Domingo logwood . . .	13.19	1.88	14.02	70.73
Monte Christo logwood, 1887 . .	14.70	1.03	14.00	70.27
Fort Liberté logwood, J. B., 1887 . .	11.84	1.03	18.00	69.13
Yucatan logwood, E. J. .	14.51	1.20	17.34	66 95
Domingo logwood, D. . .	13.71	2.14	19.30	64 85
Jamaica wood	12.10	1.30	18.00	68.60
Jamaica wood roots . . .	15.30	2.30	10.70	71.70

The decoction is pale yellow if made with distilled water, but blood-red if a calcareous water has been employed. The whole of the hæmatoxylin can only be removed with difficulty by water, but alcohol and ether extract it with facility.[1]

Hæmatoxylin,[2] $C_{16}H_{14}O_6$, is best obtained by treating the aqueous extract of logwood, or the finely powdered wood, with ether, evaporating the resultant solution to a syrup, adding water, and allowing it to stand for some days, when the hæmatoxylin is deposited in crystals, which if prismatic contain 3 *aqua*, but if granular 1 *aqua* only. A portion of the water is lost at 100°, but the whole of it can only be expelled at a higher temperature. When further heated, hæmatoxylin fuses, and at a still higher temperature decomposes and leaves a bulky carbonaceous residue. The crystals of hæmatoxylin are bright yellow, sometimes brownish externally, but the powder is yellowish-white. Its taste resembles that of licorice.

Hæmatoxylin is only slightly soluble in cold water, but more readily on heating, and is dissolved with facility by alcohol, ether, and carbon disulphide. It has the characters of a weak acid, and unites with bases to form compounds which are colorless when perfectly pure, but absorb atmospheric oxygen with great avidity, becoming first bluish and finally reddish-brown, from formation of h æ m a t e ï n and more advanced products of oxidation. The compounds of hæmatoxylin with the alkalies are best obtained by saturating a cold decoction of freshly-drilled logwood with common salt, and gradually adding caustic soda. The precipitate first formed contained the colored oxidation-products, and should be rapidly filtered off, and on again adding caustic soda a colorless precipitate of the sodium salt is obtained, which becomes rapidly colored on exposure to air.

Neutral and basic acetates of lead yield, with hæmatoxylin, bluish-white precipitates, which rapidly darken on exposure to air. Stannous chloride produces a permanent rose-colored precipitate. Alum gives a bright red color, but no immediate precipitate, though a slight blackish precipitate is formed after some time; and aluminium acetate yields a fine purple. Hæmatoxylin instantly

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[1] The amount of extract obtained from a wood is not identical with its tinctorial value.

[2] This word is often pronounced hæmat-oxylin, but such a practice is open to objection.

reduces chromic acid and potassium bichromate, yielding a deep black precipitate.

Hæmatoxylin is also used as an indicator, its tincture being exceedingly sensitive to free alkalies and alkaline salts, with which it gives a blue color, while with acids it is red. It is especially sensitive to ammonia, the faintest traces of which are sufficient to produce a blue color. Hæmatoxylin is also very sensitive to calcium carbonate.

Hæmateïn, $C_{16}H_{12}O_6$, is produced with great facility by the atmospheric oxidation of hæmatoxylin, especially in presence of an alkali.[1] It may be prepared by saturating ammonia with hæmatoxylin, and exposing the warm solution to the air. The liquid becomes deep cherry-red, and ultimately deposits granular crystals of the ammonium salt of hæmateïn. This, when decomposed by acetic acid, yields free h æ m a t e ï n as a bulky, brownish-red precipitate, which on drying becomes deep green, and exhibits a metallic lustre. Hæmateïn yields a red powder, which is sparingly soluble in cold but more readily in boiling water. It is sparingly soluble in alcohol and acetic acid and slightly soluble in ether, and dissolves in ammonia and the fixed alkalies to form solutions which are at first blue or purple, but become brown by contact with air. The a m m o n i u m   s a l t forms a deep violet powder, consisting of microscopic, transparent, four-sided prisms, which dissolve in water with a purplish, and in alcohol with a reddish-brown color. The salt loses its ammonia at 100° C., or even at the ordinary temperature over sulphuric acid *in vacuo*. Its solution yields a violet-blue precipitate with salts of copper, and a violet with stannous chloride. It reduces silver nitrate, and with ferric salts gives a black precipitate. By oxidizing agents hæmateïn is converted into brown ulmic bodies. By sulphuretted hydrogen it is decolorized, but hæmatoxylin is said not to be the product of the reduction, though it is certainly formed when sulphurous acid and certain other reducing agents are employed.

Hæmateïn is destroyed by hot sulphuric acid, but dissolves in the cold concentrated acid, with dark reddish-brown color. On adding two or three measures of glacial acetic acid very gradually to this solution, a body of the formula $C_{16}H_{11}(SO_3H)O_6$, is thrown down as an orange crystalline precipitate. This body, which is

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[1] Hæmateïn may also be prepared from hæmatoxylin by oxidation with alkaline nitrites.

apparently a sulphonic acid, is insoluble in alcohol, ether, or benzene, but slightly soluble in strong acetic acid or cold ammonia.

The reactions of an aqueous decoction of logwood are due to the simultaneous presence of both hæmatoxylin and hæmateïn.[1] Dilute acids turn the solution yellow, but with excess of a strong acid a red color is produced. Sulphuretted hydrogen decolorizes the solution of logwood, and sulphurous and carbonic acids turn it yellow. Alkalies and ammonia produce first a red, then a violet, and ultimately a brown color; while lime, baryta, and most of the hydrated oxides of the heavy metals produce blue precipitates. Stannous hydroxide behaves as a base and yields a violet lake, while stannic hydroxide reacts as an acid and turns a logwood solution red. Salts of iron yield a bluish-black coloration, a reaction which is employed for producing *ink*. Mercuric chloride yields an orange, tartar-emetic a carmine, and bismuth nitrate a fine violet precipitate with logwood solutions. Alum gives at first a yellow coloration, becoming red after a time; while aluminate of sodium yields an abundant bluish-violet precipitate, insoluble in excess of alkali. This reaction is said to be so delicate and characteristic that by means of it logwood may be detected in a mixed decoction with great facility. Another characteristic reaction of logwood is the black coloration it produces with bichromate of potassium. A good way of applying the test is to boil some white wool in a solution of potassium bichromate, containing such an amount of the salt as will correspond to 3 per cent. of the weight of the wool. The mordanted wool is then introduced in small successive portions into the hot liquid to be tested, when it will be dyed black if logwood be present, and the weight which can be thus dyed will be an indication of the amount of coloring matter. This method of assay takes cognizance both of the actual and potential coloring matter present (hæmateïn and hæmatoxylin), and, as pointed out by L. Siebold (*Jour. Soc. Chem. Ind.*, 1889), is a more rational method of examination than any based on the color produced on cotton mordanted with alumina or tin salts.

The coloring matter of logwood may be extracted by agitating the acidulated aqueous solution with amylic alcohol, or, less advantageously, with chloroform. On shaking the amylic alcohol with a saturated solution of borax, the coloring matter passes into

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[1] C. E. Avery (*Jour. Soc. Dyers, &c.*, i, 268) has patented the use of hypochlorites, nitrates, chlorates, &c., for oxidizing hæmatoxylin to hæmateïn and thus getting the full development of color without "ageing."

the latter, and may be isolated by separating the borax solution, acidulating it, and again shaking with amylic alcohol.

In commerce, logwood chips or·raspings often occur containing an abnormal proportion of *water*, from 40 to 50 per cent. being occasionally met with. 14 per cent. is the average proportion of water natural to unfermented logwood, and should be deducted in calculating the excess. An excess causes fermentation when the material is allowed to remain long in heaps, with consequent destruction of the coloring matter.

Logwood is occasionally treated with an *alkali*, such as lime water, weak soda, or stale urine, with the view of giving it a factitious strength. If so treated, the wood yields abundance of color to water, but oxidation and deterioration speedily occur. On treating such logwood with a little cold distilled water, and floating a piece of sensitive red litmus paper on the surface of the liquid, the paper will be turned blue before its color is affected by the logwood.

A rough comparative test of the tinctorial value of logwood may be made by treating 0.5 gramme of each sample with 50 c.c. of methylated spirit, agitating at intervals for an hour, and comparing the depth of color of the different tinctures.

Logwood extract is met with in commerce both in a liquid and a solid form. The specific gravity is not a reliable indication of the strength of the fluid extract, as it is liable to be raised by the addition of salt, glucose, molasses,[1] etc. The solid and paste extracts may not only contain salts, but are sometimes adulterated with farina, chestnut-bark extract,[2] etc. Treatment of the

[1] If the decolorized extract solution gives no precipitate, or a very slight one, with Fehling's solution, but after inversion with hydrochloric acid a copious precipitate of Cu_2O is thrown down, the presence of sugar by-product is evident. If the nitrogen present is over one per cent., adulteration with gum is probable. If gum is present to the amount of 8 per cent. or more, it is detected by extracting the dried and pulverized extract with strong alcohol. dissolving the residue in water, and precipitating with excess of lead acetate solution. The precipitate is filtered off and excess of lead removed by sodium carbonate. Filter, to remove lead carbonate, and to the filtrate add a tannin solution. The presence of gum is indicated by a precipitate or by considerable cloudiness.

[2] In order to detect the presence of chestnut extract in a sample of logwood extract. the following tests are made:—(1) On the addition of tartar emetic pure logwood extract is not precipitated. but chestnut extract produces a gelatinous deposit. (2) With pure extract, acid nitrate of bismuth gives a cloudiness which redissolves in excess of the reagent, and a deposit is only formed on prolonged standing; but if any tannin extract is present, the cloudiness does not disappear, and a deposit is formed in 10 minutes.

sample with methylated spirit, and observation of the intensity of
the color of the resulting tincture, is a useful method of exami-
nation.

H. Trimble (*Jour. Soc. Dyers, &c.*, i. 92) recommends that
the colorimetric assay of logwood extract should be made by treat-
ing a volume of solution corresponding to 0.001 gramme of the
dry extract with 10 c.c. of water naturally or artificially containing
" traces of calcium carbonate " and a solution of 0.002 gramme of
crystallized copper sulphate. The mixture is brought quickly to
the boiling point, and diluted with distilled water to 100 c.c.
The color of the solution is then compared with one of pure hæma-
toxylin similarly treated, or with a standard sample of logwood
extract.

The most satisfactory method of assaying logwood and logwood
extracts is by a miniature dye-test with wool and potassium bichro-
mate, as described on page 256. A known quantity of the sample
should be boiled with water, the solution strained, and diluted to
a definite volume. A standard specimen must of course be treated
in a similar manner, side by side with the sample.

To detect the presence of molasses and dextrin in logwood ex-
tracts: 1–5 grammes of extract dried at 100° C. are extracted
with absolute alcohol until a small quantity of the alcohol with
sodium aluminate gives no longer any reaction with hæmateïn ;
the alcoholic product of extraction is preserved. In the residue,
besides the substances insoluble in alcohol which occur in extracts,
is contained the sugar of the molasses and dextrin originally
present in the extract.

As a normal extract may contain 0.25–0.5 per cent. grape sugar,
but never cane sugar, its detection in the residue after the alco-
holic extraction is the surest proof of the presence of molasses; in
the same manner, from a surplus over $\frac{1}{2}$ to 1 per cent. starch sugar
or grape sugar, the presence of a substance containing starch sugar
or grape sugar may be inferred.

With the exception of indigo, logwood is, perhaps, the most
important and indispensable of dyeing matters. It does not dye
cotton without a mordant, and wool merely acquires a useless drab-
tint. Hence the employment of logwood in dyeing depends on
the color-lakes which it forms with metallic oxides.

With aluminium mordants, logwood yields deep violet-gray
shades. With ferrous salts it gives a bluish-black, and with ferric
salts a brown-black shade, while a mixture of the two yields a finer

black than either separately. With chromates, logwood yields a black color, which on exposure to light gradually takes a greenish shade. Logwood is used chiefly for dyeing black in conjunction with potassium bichromate. It likewise yields blues, which resemble those produced by indigo, but are not so fast. It is also used in dyeing leather, and in printing calico brown, slate, lilac, gray, &c.

Fibres dyed black by logwood leave on ignition an ash containing oxide of chromium, sometimes mixed with alumina or oxide of copper or iron. The dyed fabric is turned red by moderately concentrated hydrochloric acid (tannin blacks are altered, but not reddened), and if the reddened spot be pressed, while still moist, against a piece of filter-paper, it produces a cherry-red stain, which turns blue if touched with a glass rod moistened with aluminate of sodium. Logwood violets and blues leave on ignition an ash containing alumina. With hydrochloric acid they behave like logwood black. When placed in milk of lime, and subsequently washed with soap, the color is discharged. All logwood colors are readily bleached by chlorine and hypochlorites.

If a fibre dyed with logwood (especially the blues) be boiled with glacial acetic acid the coloring matter is dissolved, and the solvent when cold has a rose-red color, changing to yellowish-red on warming. On adding ether and sufficient water to cause separation of an ethereal layer, any indigo will remain in the ether or separate at the junction of the two liquids, while in presence of any quantity of logwood the lower layer will be reddish-blue. If the amount present be insufficient to produce this effect, the logwood will still be detected on adding a few drops of hydrochloric acid. This will color the aqueous liquid a beautiful red, while at the same time it will decolorize that portion of the logwood coloring matter which was taken up by the ether. In the presence of cotton-blue or indigo-carmine, the acetic solution should be separated from the ethereal layer and shaken with amylic alcohol. This dissolves the logwood coloring matter, which can be extracted by agitating the amylic alcohol with a saturated solution of borax, and thus obtained pure.

Brazil Wood is derived from the *Cæsalpinia Brasiliensis*, a tree growing in the forests of Brazil. The red dyewoods known in commerce as *peach-wood, sapan-wood, Lima-wood, Bahia-wood, &c.,* are all the products of various species of *Cæsalpinia*, and yield very similar shades of colors on fabrics, either when employed

alone or with mordants. They appear, also, to contain the same g l u c o s i d e, which is decomposed by peculiar ferments, or by boiling with dilute acids into a glucose and the coloring matter b r a z i l i n, a substance which has been found in large crystals in casks in which extract of sapan-wood had been kept. The crust obtained in the manufacture of brazil-wood extract contains much brazilin and its lime-compound. If treated with dilute hydrochloric acid, and then boiled with a mixture of one part of alcohol and eight of water, a solution is obtained from which brazilin crystallizes on cooling.

Brazilin, $C_{16}H_{14}O_5$, may be obtained from brazil-wood by the method employed for the preparation of hæmatoxylin from logwood. When pure it forms colorless hydrated crystals, which become anhydrous at 130° C. It dissolves in water, alcohol, and ether. Brazilin presents a close resemblance to h æ m a t o x y l i n, $C_{16}H_{14}O_6$, from which it differs only by an atom of oxygen.[1] On exposure to the air the solution acquires a bright red color from the formation of b r a z i l e ï n. This change is greatly facilitated by the presence of alkalies.[2] Acetyl- and bromo-derivatives of brazilin have been obtained.

On adding chromic acid or potassium bichromate to an aqueous solution of brazilin, a dark brown coloration is produced, and a very dark crimson lake separates on standing. This substance, which is apparently a compound of brazilin and chromic oxide, is readily decomposed by dilute acid.

Brazileïn, $C_{16}H_{12}O_5$, is produced by the oxidation of brazilin in alkaline solution, and may be prepared in a manner similar to that used for obtaining h æ m a t e ï n, $C_{16}H_{12}O_6$, to which it presents a close analogy. Brazileïn forms minute crystals, having a gray lustre. The powder is reddish-brown. It is very slightly soluble in cold, but more readily in hot water. The solution is yellowishpink, with a greenish-orange fluorescence. On addition of an

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[1] According to E. K o p p, brazilin has the formula $C_{22}H_{18}O_7$, which, if correct, would render it probable that brazilin was the r e s o r c i n o l e t h e r o f h æ m a t o x y l i n, $C_6H_4 \begin{cases} OH \\ O.C_{16}H_{13}O_5. \end{cases}$ From the investigations of H e r z i g and S c h a l l it would appear that *brazilin* and *hæmatoxylin* behave analogously to the compounds of the *xanthon* and *fluoran* groups, and that they are probably hydroxyl derivatives of these mother substances.

[2] Brazilin serves as a very sensitive indicator for titrating such alkaloids as quinine, atropine, brucine, and cocaine; it gives a purplish-red color with alkalies and a yellow color with acids.

alkali the solution becomes carmine-red, changing to brown on exposure to air. With concentrated sulphuric, hydrochloric, and hydrobromic acids, brazileïn reacts to form crystallizable compounds, which have greater tinctorial powers and are faster on the fibre than brazileïn itself. Boiling with zinc-dust or acid sulphite of sodium reduces brazileïn to b r a z i l i n.

An aqueous decoction of brazil-wood, or any of the allied woods, becomes yellow or orange on addition of an acid, the shade of color depending on the relative proportions of brazilin and brazileïn present. If the solution be strong, yellow or red crystals will probably separate on standing. With excess of strong hydrochloric acid, brazil-wood solution becomes a bright pink, but the coloration disappears on adding water. Ammonia, caustic alkalies, and carbonates of the alkali-metals turn the solution crimson-red, this color gradually changing to brown on exposure to air. Potassium bichromate reacts as with brazilin. Neutral lead acetate gives a slight reddish precipitate containing oxidation-products. The filtered liquid dyes a deeper shade than the original solution. Basic acetate of lead gives an abundant bluish precipitate with brazil-wood solution.

Brazil-wood and the commercial extract are liable to the same kind of adulterations as logwood and its preparations, and may be examined by exactly similar methods, except that for the dyeing test twice the quantity of brazil-wood should be employed, as it is not so rich in brazilin as logwood is in hæmatoxylin.

Brazil-wood is used in calico-printing and dyeing, and yields colors similar to those obtainable with cochineal or alizarin. Thus when mordanted with alumina it gives red, with iron grayish-violet or black, and with a mixture of the two, brown. Stannic chloride gives a red, and chromates an olive shade.

When fixed on fabrics, reds produced by brazil-wood are turned violet-blue by alkalies, while acids change them to yellow and red, and give a pink solution. They are bleached by chlorine and hypochlorous acid, and are discharged by boiling with soap solution bluish-red, a character which distinguishes them from the alizarin reds. When immersed in succession in hydrochloric acid and in lime-water, fibres dyed red with brazil-wood are changed to violet, and the latter color can then be removed by boiling with soap. Concentrated sulphuric acid alters brazil-wood red to deep cherry-red, while it changes a cochineal red to an orange-yellow. On ignition, fibres dyed with brazil-wood leave a residue contain-

ing alumina, oxide of tin, etc., according to the mordant employed for fixing the color.

SANTAL WOOD or SANDAL WOOD, BARWOOD, CALIATOUR WOOD, and CAMWOOD differ from brazil-wood and its allies in their more resinous characters, and are often known as "close woods." They yield faster dyes than the "open woods," but the insolubility of the coloring matters prevents them from being used in the form of extracts.

Santalin, $C_{15}H_{14}O_5$ (?), the coloring principle of santal wood, seems to be identical with that of barwood, and probably with that of camwood. It appears to be developed by age, being absent from the young branches, but existing in large quantities in the trunk. The chemistry of santalin is very imperfectly understood, and the formula is uncertain. Santalin is best extracted by boiling crushed santal wood with water to remove the tannin, heating the insoluble residue with a solution of borax, and saturating it with lime until the coloring matter is entirely removed. The filtered liquid is then treated with sulphuric or hydrochloric acid until no further precipitate is obtained. The voluminous red precipitate is filtered off and dissolved in boiling alcohol, when the santalin separates as a red crystalline powder as the solution cools. Santalin is insoluble in water, but soluble in alcohol, ether, and acetic acid. It dissolves in ammonia, fixed caustic alkalies, and carbonates, phosphates, and borates of the alkali-metals with violet-red color, and is reprecipitated in red flakes on acidulating these solutions.

A. Z a n d e r (*Jour. Soc. Dyers, &c.*, iv. 496) has recently proposed the employment of a s a n t a l i n - s u l p h o n i c   a c i d. This is prepared by treating santal wood, or one of the allied woods, with a warm solution of borax, sodium phosphate, or carbonated or caustic soda, and precipitating the crude santalin from the liquid by means of an acid. The santalin is then warmed with ordinary concentrated or fuming sulphuric acid, until a sample ceases to be precipitated on dilution with water. The product is then poured into a cold saturated solution of common salt, and the precipitated coloring matter washed and dried. Santalin-sulphonic acid and its sodium salt occur in commerce as grayish-brown powders, readily soluble either in hot or cold water. The solution gives no characteristic reactions. It is best applied in an acid bath containing sodium sulphate, and produces shades of color much yellower than, but equally deep and fast with, those obtained with the original dye-wood.

Santal Wood or *Sandal Wood*, called also *sanders wood* or *red sanders*, is imported in large billets, which are very dense (sp. gr. 1.014) and compact, and of blackish-brown color externally, while the interior is red. The fibers occur in alternate layers running in opposite directions, and hence when planed the wood exhibits alternately a polished and a rough torn-up surface. Powdered santal wood is lighter than water, has an aromatic taste, and an odor like that of orris-root. It yields to alcohol about 16 per cent. of a coloring matter which is insoluble in water.

Santal wood is chiefly used on the Continent, where it is employed to give a bottom to woolen cloth which is afterwards to be dyed with indigo. The fine color called *bleu de Nemours*, obtained in this manner, has a purple hue by reflected light. Santal wood is also used for dyeing woolen and cotton a dark red, which is changed to a rich brown by a chromate-bath. It produces dark browns with sumac and light browns with fustic.

Barwood is allied to santal wood. It is compact, and of an orange color when polished. It generally occurs in the form of raspings, as a rough, harsh, and odorless powder. Boiling water takes up about 7 per cent. of coloring matter, which on cooling is almost entirely deposited as a reddish powder. The coloring matter is soluble in alcohol, but the whole amount, averaging 23 per cent., can only be extracted from the wood by repeated treatment. The coloring matter dissolves in soda or ammonia with violet-red color, and is reprecipitated in red flakes on acidulating the solution.

Barwood is employed to produce mock turkey-reds on cotton, which are distinguished from the alizarin-dyed goods by yielding part of their color to soap, and at the same time assuming a purple hue. It is also used for dyeing woolens brown and other dark tints.

Cam Wood or *Kambe Wood* yields its coloring matter to water much more freely than santal and barwood, but is not sufficiently soluble to yield an extract. It is used in a manner similar to barwood, and is regarded as producing brighter and faster colors.

An alcoholic extract of santal or barwood is rendered opalescent by copious dilution with water. The fixed alkalies redissolve the precipitate, the liquid acquiring a dark claret color. Caustic alkalies change the original alcoholic solution to crimson or violet, while lime water produces an abundant reddish-brown precipitate. Dilute acids heighten the color of alcoholic solution of santal or

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barwood to a deep cherry-red; while chlorine decolorizes the tinc-
ture, with formation of an ochre-like precipitate which rises to the
surface of the liquid. The tincture of santal or barwood yields
with stannous chloride a blood-red, and with stannic salts a brick-
red precipitate; with ferrous salts a violet coloration and abundant
violet precipitate; with ferrous salts an intense brownish-red colo-
ration and precipitate; and with tartar-emetic an abundant, dark
cherry-red precipitate. Salts of aluminium only render the liquid
turbid, while lead salts give a dark violet, gelatinous precipitate.
The last two reactions distinguish santal- and bar-wood from *cam-
wood*, an alcoholic extract of which gives a beautiful red coloration
with salts of aluminium, and a bright orange-red precipitate with
salts of lead.

Santal-, bar-, and cam-wood are chiefly used in wool-dyeing,
together with other dyewoods, such as logwood and old fustic, for
producing various shades of brown, olive, drab, &c. They have
also a limited application in cotton-dyeing, but are not used for silk.

Fibres dyed with santal- or bar-wood are not changed by hydro-
chloric acid, but if of wool are turned dark olive by nitric acid.
Alcohol is colored red, as also is an acid solution of stannous
chloride, the color of the fibre remaining unchanged. Caustic
soda and ammonia turn the fibre purplish or brownish without
yielding a colored solution. When boiled with ferrous sulphate,
cloth dyed with santal-wood becomes violet.

ALKANET consists of the cortical parts of the root of *Anchusa
tinctoria*. The coloring matter called *alkannin* may be prepared by
boiling the root with water to remove all soluble matter, drying it,
and then exhausting with alcohol. The solution, which has a
violet color, is slightly acidulated with hydrochloric acid and
evaporated to dryness. The residue is treated with ether, which
on evaporation leaves the coloring matter as a dark red, resinous
substance. According to C a r n e l u t t i and N a s i n i (*Jour. Chem.
Soc.*, xl. 53), the product so obtained is contaminated with a
reddish-brown acid. The coloring matter is best obtained pure
by extracting alkanet root with dilute potash solution, and agitat-
ing the solution with ether to remove the above-mentioned im-
purity. On saturating the alkaline liquid with carbonic acid the
alkannin is precipitated, and may be purified by solution in ether.

Alkannin, Anchusin, or *Anchusic Acid*. This body, of which
the formula is probably either $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$, is a reddish-
brown resinous substance of metallic lustre. It is insoluble in

water, but soluble in alcohol, glacial acetic acid, ether, chloroform, carbon disulphide, turpentine, and fixed oils. The alcoholic solution is crimson, and is unchanged by exposure to light or continued boiling. It gives a blue coloration with alkalies (restored to crimson by acids),[1] a bluish-violet precipitate with aluminium acetate, a crimson precipitate with stannous chloride, and a purple precipitate with stannic chloride. Lead acetate produces a blue, and iron salts a violet precipitate. Alkannin forms a diacetyl-derivative which crystallizes from glacial acetic acid in brownish-yellow grains. Alkannin is evidently a derivative of m e t h y l-a n t h r a-c e n e, $C_{15}H_{12}$, as that hydrocarbon is formed when the coloring matter is distilled with zinc-dust. In its tinctorial properties and absorption-spectrum, anchusin resembles q u i n-a l i z a r i n.

The most characteristic test for alkanet and alkannin is the absorption-spectrum. The solution in amylic alcohol gives the best results, and exhibits three equidistant bands in the blue-green. On adding ammonia these give place to two bands, one nearly coincident with and the other on the red side of the D line.

Alkanet root may be assayed by treating it with ether, which should extract not less than 5 per cent. of coloring matter. Alkanet was formerly used for dyeing various shades of violet, lilac, lavender, and yellow, but has been superseded for such purposes. It is used for staining wood crimson, and is employed in perfumery for coloring oils and pomades. An alkaline solution is sometimes used to color syrups. Tincture of alkanet forms a very good substitute for litmus.

SAFFLOWER consists of the bloom or petals of a plant resembling the thistle, indigenous to Egypt and the Levant, and cultivated in other countries. It varies much in quality, the Egyptian being the richest in coloring matter, and after that the Indian and Chinese. The color of good safflower is a fiery red; a dull red color is an indication of bad preparation.

Safflower contains two yellow coloring matters, one of which is soluble in cold water, and exists in considerable proportion (26 to 36 per cent.); the other is insoluble in water, but dissolves in alkaline liquids. Besides these, safflower contains a small proportion of a red coloring matter called c a r t h a m i n, which is the only constituent of value. The proportion of insoluble yellow coloring matter varies inversely with that of carthamin.

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[1] Paper impregnated with an alcoholic solution of alkannin forms the so-called Bœttger's Test Paper. It is very sensitive to free alkalies and alkaline salts and particularly to ammonia, the slightest traces of which color the paper green.

Carthamin, $C_{14}H_{16}O_7$, the red coloring matter of safflower, forms only from 0.3 to 0.6 per cent. of the weight of the flowers. To prepare it, safflower is washed with cold water till no more soluble yellow coloring matter is removed, after which it is treated with water and 15 per cent. of its weight of crystallized sodium carbonate. The solution is strained from the insoluble portion, cotton yarn immersed in it, and the liquid acidulated with citric acid. The cotton takes up the carthamin and an accompanying yellow coloring matter. When washed and treated with a weak solution of sodium carbonate, the carthamin dissolves, while the yellow dye remains fixed on the cotton. On acidulating the solution with tartaric acid, the carthamin is thrown down as a bright red, amorphous precipitate, which, when mixed with a little water, forms the *safflower extract* or paste of commerce.[1] The product may be further purified by solution in alcohol and reprecipitating it by adding water.

Carthamin is insoluble in water or ether, but readily soluble in alcohol. The cherry-red alcoholic solution dyes silk without a mordant, and when allowed to evaporate on glass leaves a varnish which appears red by transmitted light and a beautiful beetle-green by reflected light. On addition of an acid, the alcoholic solution of carthamin becomes yellow, and alkalies also turn it yellow or orange. The coloring matter is consequently very unstable, and even undergoes rapid alteration on exposure to air or when boiled with alcohol or water.

Carthamin has feeble acid characters. The ammonium salt yields, with stannic chloride, a yellowish-brown precipitate, with ferric chloride a brownish-red, and with mercuric chloride a red precipitate.

Carthamin dissolves with red color in strong sulphuric acid, probably forming a sulphonic acid, for the solution is not precipitated on addition of water.

Safflower is best assayed by a miniature dyeing operation, and by an application of the method already described for detecting and separating any objectionable yellow coloring matter.

Safflower is employed to dye silk, cotton, and linen various shades of pink and red. On fabrics dyed with annatto it produces a scarlet. The use of safflower has much decreased of late years,

[1] If the paste be triturated with French chalk and the mixture dried, a product is obtained which is employed as a *rouge*.

owing to the competition of the coal-tar colors, but it is still employed for coloring red tape.

On the fibre, a rose, pink, or crimson color due to safflower is immediately turned pale yellow by a single drop of alkali, and the color is then destroyed by any further treatment. Weak acids do not affect the color, but strong acids, chlorine, and sulphurous acid bleach it at once. Alcohol has no action, but ammonia changes safflower pink (on cotton) to a flesh-tint, and ammonium sulphide decolorizes it.

Yellow Dyes of Natural Origin.

The yellow coloring matters of natural origin which receive practical applications are all of vegetable derivation. They are of very various origin and character, as will be seen from the tabulated list of the more important on the next page.

A number of other vegetable coloring matters might be enumerated, including *Chinese yellow*, from *Gardenia grandiflora ; Chrysophan*, from Goa powder ; coloring matters of rhubarb, barberry root and carrot, and many others.

QUERCITRON BARK, as met with in commerce, is a mixture of fibres and fine powder of a yellow or buff color. The articles imported respectively from Philadelphia, New York, and Baltimore rank as distinct qualities, the first being generally preferred.

Quercitrin, the yellow coloring principle of quercitron, was obtained by Chevreul by boiling the bark with water, and allowing the solution to stand, when the quercitrin is deposited in crystals. Bolley prepares it by boiling the bark with alcohol, precipitating the tannin (quercitannic acid) by gelatin, concentrating the filtrate, and recrystallizing the quercitrin which separates from boiling alcohol. Quercitrin is most readily prepared by boiling the preparation of quercitrin known as *flavin* with water, and cooling the filtered liquid. Quercitrin forms pale yellow, rhombic plates, which are odorless, having a somewhat bitter taste, and a feeble acid reaction. It is only slightly soluble in cold water or ether, more readily in boiling water (1 in 25), and easily in alcohol. Ammonia and the fixed alkalies dissolve quercitrin readily, with greenish-yellow color. The ammoniacal solution rapidly oxidizes, and turns brown on exposure to air. The aqueous solution of quercitrin gives a reddish-yellow precipitate with baryta water; a beautiful yellow color with alum; flocculent yellow precipitates with the acetates of copper and lead ; and an

olive-green coloration and gradual precipitate with ferric sulphate. Nitric acid colors quercitrin orange-red.

Quercitrin is a glucoside, suffering hydrolysis when boiled with dilute sulphuric acid, with formation of q u e r c e t i n and a sugar-like body. The formula of quercitrin is somewhat uncertain, and it is doubtful whether different observers have always

COMMERCIAL NAME.	SOURCE.		COLORING PRINCIPLE.	
	Botanical.	Geographical.	Name.	Formula.
Quercitron	Bark of *Quercus nigra* or *Q. tinctoria.*	North America.	Quercitrin. Quercetin.	$C_{36}H_{38}O_{20}$ $C_{24}H_{16}O_{11}$
Old Fustic; Yellow Brazil wood.	Wood of *Morus tinctoria.*	West Indies; South America.	Moric acid. Morintannic acid.	$C_{12}H_{10}O_6$ $C_{13}H_{10}O_6$
Young Fustic; Fustet wood.	Wood of *Rhus Cotinus.*	West Indies; Levant, South Europe.	Fustin or Fisetin.	$C_{23}H_{16}O_9$
Weld.	Leaves, &c., of *Reseda luteola.*	France, &c.	Luteolin.	$C_{20}H_{14}O_8$
Persian Berries; Yellow Berries.	Various species of *Rhamnus.*	Spain, France, Persia, Turkey, &c.	Xanthorhamnin.	$C_{48}H_{66}O_{27}$
Saffron.	Stigmata of flower of *Crocus sativus.*	Austria, Spain, France.	Crocin. Crocetin.	$C_{44}H_{70}O_{28}$ $C_{34}H_{46}O_9$
Annatto.	Pulpy parts of *Bixia Orellana.*	Mexico; South America.	Bixin.	$C_{28}H_{34}O_5$
Turmeric.	Underground stem of *Curcuma tinctoria.*	East Indies; China, Barbadoes.	Curcumin.	$C_{14}H_{14}O_4$
Gamboge.	Gum resin from *Garcinia morella.*	Siam, Cochin China, Ceylon.	Gambogin.	$C_{30}H_{35}O_6$

worked on the same body. According to H l a s i w e t z and P f o u n d l e r, several kinds of quercitrin exist, all of which yield quercetin on treatment with dilute acids, but differ as to the kind of sugar simultaneously produced. But it seems more probable that quercetin and isodulcite are constant products of the hydrolysis, though the proportions formed depend on the origin of the glucose. Thus while r u t i n, $C_{24}H_{50}O_{25}$, contained in the leaves of *Ruta graveolens* and *Polygonum fagopyrum*, splits on hydrolysis into one molecule of quercetin and *one* of isodulcite, quercitrin yields one of quercetin and *two* of i s o d u l c i t e (vol. ii.), according to the following equation:—

$$C_{36}H_{38}O_{20} + 3H_2O = C_{24}H_{16}O_{11} + 2C_6H_{12}O_5, H_2O$$
$$\underset{\text{Quercitrin.}}{} \qquad \underset{\text{Quercetin.}}{} \qquad \underset{\text{Isodulcite.}}{}$$

Quercetin, $C_{24}H_{16}O_{11}$,[1] or its glucoside, is found in a great variety of plants. It forms slender needles of a bright yellow color, which are tasteless, and insoluble in cold water. Quercetin is but slightly soluble even in hot water (1 in 280), but dissolves readily in alcohol and in acetic acid, and sparingly (1 in 125) in ether. In alkalies it dissolves with orange-yellow color, and a crystalline compound, containing $C_{24}H_{16}O_{11}, K_2O$, has been obtained by dissolving quercetin in a concentrated solution of potassium carbonate. An alkaline solution of quercetin becomes dark brown when treated with sodium-amalgam, the color gradually changing to yellow. The alcoholic solution of quercetin yields orange precipitates with calcium, barium, and lead salts; gives an orange coloration with stannic chloride, and a green with ferric chloride.

Quercetin dissolves in strong sulphuric acid, apparently forming a s u l p h o n i c   a c i d, and the solution dyes wool a fast yellow without a mordant. A   d i - a c e t y l - d e r i v a t i v e has also been obtained.

If 1 part of quercetin be treated with 3 parts of caustic potash and 1 of water, and the whole evaporated to dryness, the quercetin is split up with formation of p a r a d a t i s c e t i n, $C_{15}H_{10}O_6$, q u e r c e t i c   a c i d, $C_{15}H_{10}O_7$,   and   p h l o r o g l u c o l, $C_6H_6O_3$. By prolonging the treatment with potash, or by treating quercetin at once with the fusing alkali, the quercetic acid is further decomposed into p r o t o c a t e c h u i c   a c i d, $C_7H_6O_4$,   and   q u e r c i - m e r i c   a c i d, $C_8H_6O_5$, which latter takes up oxygen and again splits up into protocatechuic acid and carbon dioxide.

Quercetin is easily decomposed when its acidulated aqueous solution is boiled.

When a dilute alcoholic solution of quercetin containing silver

[1] J. H e r z i g (*Jour. Chem. Soc.*, 1. 251) has given reasons for doubting the accuracy of this formula. From a study of its alkyl and acetyl derivatives, he ascribes to quercetin the formula $C_{17}H_{10}O_7$, which is structurally represented by:
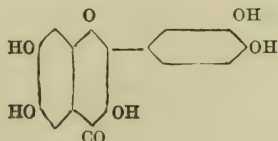
nitrate is shaken with three volumes of ether, the latter acquires a crimson color rapidly fading with deposition of metallic silver.

If an alcoholic solution of quercetin be acidulated with hydrochloric acid and treated with sodium amalgam, the liquid assumes a fine purple color, and on concentration yields red prisms, which dissolve in alcohol and a little alkali with green color, the solution being readily reoxidized with formation of quercetin on exposure to the air.

Besides quercitrin, quercitron bark contains q u e r c i t a n n i c a c i d.

Flavin is the commercial name of a preparation of quercitron produced by acting on the bark with sulphuric acid, and hence contains woody fibre with more or less quercitrin, quercetin, and isodulcite. In some cases it consists of nearly pure quercitrin, and in others of quercetin. A good quality of flavin has about sixteen times the coloring power of quercitron bark, but very inferior specimens are sometimes met with. *Aurantine* and '' patent bark '' are preparations similar to flavin.

A freshly-prepared decoction of quercitron bark is transparent, and of a dull orange-red color, but after a time it becomes turbid, gives a yellow crystalline deposit, and the supernatant liquid gradually becomes gelatinous and acquires a blood-red color. A freshly made solution is deepened in color by alkalies and lime-water, the latter reagent also producing a brownish-yellow flocculent precipitate. Alum brightens the color, and forms a light precipitate only. Stannous chloride gives a brown and stannic chloride a yellowish precipitate. Gelatin produces a reddish flocculent precipitate, and chlorine also precipitates abundant flocks, an excess of the reagent decolorizing the liquid. Iron salts color the solution of quercitron green, an olive-brown flocculent precipitate being subsequently formed.

Flavin and quercitron bark are chiefly used for dyeing woolen and mixed fabrics, tin being usually the mordant employed. Flavin is largely used in conjunction with cochineal or lac-dye for producing scarlet. Samples of flavin or quercitron are best assayed by a miniature dye-test.

Fibres dyed with quercitron bark yield a yellow solution with hydrochloric acid, but the color of the fibre is little affected. Caustic alkalies behave similarly. Nitric acid turns the fibre light brown, and it becomes olive when boiled with ferric chloride, and orange with lead acetate. Alcohol has no action, and the color is

little affected by ammonia or an acid solution of stannous chloride, though the solution becomes yellow in each case.

Old Fustic, also called *yellow wood,* contains two peculiar principles, known respectively as m o r i n or m o r i c a c i d, and m o r i n t a n n i c a c i d or m a c l u r i n.   To obtain these bodies in a pure state, rasped fustic is boiled with water and the decoction concentrated to a syrup.   The crystalline deposit which forms in a few days is washed rapidly with cold water and pressed.   On treatment with boiling water, morintannic acid is dissolved, while calcium morate remains insoluble.   The morintannic acid is obtained by concentrating the solution, and crystallizing the coloring matter from water acidulated with hydrochloric acid.   The calcium morate is decomposed by dilute hydrochloric acid, and the residue taken up by alcohol, from which solution, on addition of two-thirds of its volume of water, the morin is deposited in yellow needles.[1]

Morin or *Moric Acid,* according to B e n e d i k t and H a z u r a, probably contains $C_{13}H_8O_6$.[2]   It crystallizes in colorless needles containing 1 *aqua.*   It is nearly insoluble in water and carbon disulphide, slightly soluble in ether, and freely in alcohol.   In solution of caustic alkalies, carbonates, borates, and phosphates, it dissolves with a yellow color, and is reprecipitated on addition of an acid.   Ferric chloride gives an olive-green coloration with the alcoholic solution of moric acid, while yellow precipitates are produced by salts of tin, lead, zinc, and aluminium, and a dark green precipitate by supric sulphate.   If an alcoholic solution of moric acid be acidulated with hydrochloric acid and treated with sodium amalgam, it acquires an intense purple color, and if then separated

[1] Morin may also be prepared by mixing fustic extract with an equal volume of water and a little hydrochloric acid, decanting the clear liquid, and repeating the treatment till the washings are no longer yellow.   The residue of crude morin is pressed. powdered, and dried in the air.   It is then dissolved in hot alcohol, and one-tenth of hot water added, when free morin separates on cooling.

[2] H e r z i g (*Ber.* xxviii. 293) ascribes to morin the following formula:
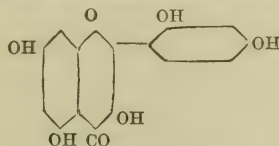
It is supposed to be quercetin in which the catechol nucleus has been displaced by a resorcinol group.

from the excess of the amalgam and concentrated, purple crystals are obtained of i s o m o r i n, a body said to be isomeric with morin.[1] The solution of this body becomes green on treatment with an alkali, and morin is gradually reproduced in the cold and rapidly on boiling. A solution of isomorin, when treated with alum, becomes intensely fluorescent, and on dilution appears yellow by transmitted and uranium-green by reflected light. The alcoholic solution of moric acid itself becomes highly fluorescent on addition of a minute proportion of alum (1:8000), a character which distinguishes it from morintannic acid, and has been suggested by Goppelsroeder as a delicate test for aluminium. When fused with caustic potash morin yields r e s o r c i n o l, p h l o r o-g l u c o l, and other products.

Moric acid presents a close analogy to quercetin in many of its characters and reactions.

Morintannic Acid or *Maclurin*, $C_{13}H_{10}O_6 + H_2O$, forms a pale yellow crystalline powder, freely soluble in water, and soluble also in alcohol, wood spirit, and ether. It becomes anhydrous at 130° and melts at 200° C. On boiling with concentrated caustic potash lye, or heating at 120° with dilute sulphuric acid, it splits up into p r o t o c a t e c h u i c a c i d and p h l o r o g l u c o l. With ferric chloride, morintannic acid yields a greenish or greenish-black precipitate. When boiled with hydrochloric acid it yields r u f i-m o r i c a c i d, a substance forming brick-red crystals and dissolving in ammonia with purple coloration.

On heating a moderately concentrated solution of morintannic acid with zinc and diluted sulphuric acid, it rapidly acquires a red color, which gradually changes to orange, and then contains p h l o r o g l u c o l and m a c h r o m i n, $C_{14}H_{10}O_5$. The latter body crystallizes in tufts of slender needles, only slightly soluble in water or alcohol, but more readily in ether. Both crystals and solutions of machromin become blue on exposure to air or treatment with oxidizing agents. On adding hydrochloric acid the solution yields an amorphous blue precipitate, and with ferric or mercuric chloride a beautiful violet coloration, gradually changing to blue. In strong sulphuric acid, maclurin dissolves with an orange color, changing to an intense green on heating. The color is unchanged by dilution, but becomes purple on adding an alkali. The blue substance produced by the action of oxidizing agents on

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[1] B e n e d i k t and H a z u r a (*Jour. Chem. Soc.*, xlvi. 1179) failed to obtain the isomorin of Hlaziwetz and Pfoundler.

machromin is said to contain $C_{14}H_8O_5$.   It is best obtained by the employment of excess of ferric chloride, washing the blue precipitate which is formed, and, after drying, washing it with ether. It dissolves in alcohol to form a solution which is decolorized by reducing agents.

A decoction of old fustic has a bitter, astringent taste.   Alkalies and lime-water change the color to a reddish-brown.   Acetic acid renders the decoction paler and brighter, and sulphuric, nitric, and oxalic acids produce slight precipitates.   Chlorine-water produces a slight precipitate and reddish coloration, which is destroyed by excess.   Alum gives a bright yellow precipitate with fustic decoction; stannous chloride, lead acetate, and gelatin yield golden or orange-yellow precipitates.   Ferric sulphate produces an olive-brown coloration, and on standing a brownish-black precipitate falls.

Old fustic with an alumina mordant dyes wool yellow, and with salts of iron olive-green.   Brighter colors can be obtained if the morintannic acid be first removed by gelatin.   The yellows produced by fustic become orange on exposure to air and light, and hence it is now rarely employed alone; but when mordanted with potassium bichromate, it is largely used for the yellow constituent of browns, jet-blacks, and greens.

Extract of fustic is liable to be adulterated with dextrin, molasses, zinc sulphate, alum, glycerin, sugar, turmeric, aniline

Reagent.	Turmeric.	Fustic.
Stannous chloride.	Reddish precipitate.	Light yellow precipitate.
Acetate of lead.	Chestnut brown.	Reddish yellow.
Ferric sulphate.	No precipitate, solution colored brown.	Black precipitate; solution colored brown, afterwards turning olive green.
Caustic alkalis.	Brown coloration.	Dark orange coloration, but no precipitate.
Mineral acids.	Red coloration; no precipitate; on diluting the coloration disappears, and the dyestuff separates out in yellow flakes.	A light yellow precipitate is formed.

dyes, and alizarin orange. The alum and zinc sulphate may be detected in the ash. Turmeric is detected by its property of dyeing unmordanted wool; if alum were present, however, fustic would also dye directly, and the above reactions may be carried out to distinguish between turmeric and fustic.

The difference in the behavior of quercitron and fustic extracts towards alum and tin salt affords us some points for the possible detection of quercitron in extract of fustic. A slip of white woolen cashmere, 10 cm. by 20 cm. dyed in a mixture of 0.5 grm. extract, 0.2 grm. alum, 0.5 grm. stannous chloride, 0.5 grm. oxalic acid in 1 litre water, if contrasted with dye-test of an extract adulterated with quercitron will give different results, which difference manifests itself by the greater intensity of color of the adulterated extract. If a swatch of the same size be dyed in the extracts under comparison, but with alum mordant alone, the adulterated extract will give weaker colorings than the pure extract of fustic.

The determination of saccharine admixtures, such as molasses, syrup, dextrin, is carried out in an analogous manner as stated when dealing with logwood extracts; that is, by extracting the products with absolute alcohol, and determining the sugar or dextrin in the residue.

Fibres dyed with old fustic become orange on treatment with hydrochloric acid, and yield an orange solution. Nitric acid turns them pale yellow. By alkalies and ammonia the fibre is little changed in color, though in the latter case the liquid is colored yellow. An acid solution of stannous chloride changes the fibre to orange, the solution being colorless. Heated with ferric chloride, the color of the fibre is changed to olive, and when boiled with aluminium acetate a yellow solution is obtained, exhibiting a bluish-green fluorescence.

Young Fustic or FUSTET WOOD, notwithstanding its name, is derived from quite a different source from old fustic. It occurs in commerce in small logs or crooked branches, that imported from the Antilles and the West Indies being the finest quality.

According to J. S c h m i d t (*Jour. Soc. Dyers, &c.*, ii, 148), fustet wood contains a substance which is easily broken up by the action either of dilute acids or alkalies into a kind of t a n n i n (probably sumac-tannin) and the glucoside f u s t i n. The red and brown coloring matters described by older investigators were probably oxidation-products or phlobaphenes of this tannin. The

fustin-tannide may be prepared by treating young fustic with water, precipitating impurities by an acetic acid solution of lead acetate, and extracting the filtrate with acetic ether. It forms yellowish-white needles, easily soluble in water, alcohol, and ether. The solution gives with ammonia brown, and with potash a brownish-red coloration, and reduces Fehling's solution. When dissolved in a little warm glacial acetic acid, and the solution diluted with water, yellowish-white needles of the glucoside f u s t i n are obtained. This substance is readily soluble in boiling water, alcohol, and alkalies, but only sparingly in ether. With lead acetate it gives a yellow and with cupric acetate a brownish-yellow precipitate, in both cases readily soluble in acetic acid. Ferric chloride gives a green coloration, changing through violet-blue to red on adding dilute soda. When warmed with dilute sulphuric acid, fustic is gradually decomposed into a s u g a r and f i s e t i n.

Fisetin, $C_{23}H_{16}O_9$, may be obtained more readily from the commercial extract of fustic known as *colinin*, which is prepared by extracting the wood with very dilute caustic soda and evaporating the solution. Fisetin crystallizes from dilute alcohol in small, lemon-yellow prisms. It is sparingly soluble in ether, benzene, petroleum spirit, chloroform, and boiling water, but readily in methyl and ethyl alcohols, and in ethyl acetate. Fisetin does not melt below 360°, but may be partially sublimed in small needles. Fuming sulphuric acid dissolves it with formation of a sulphonic acid. Alkalies and alkali-metal carbonates turn an alcoholic solution of fisetin brownish-red, and render it fluorescent. The absorption-spectrum is not characteristic. An alcoholic solution of fisetin gives a brilliant orange-red precipitate with lead acetate, an orange-yellow with stannous chloride, and a brown precipitate with cupric acetate. The precipitates in each case are readily soluble in acetic acid. Fisetin reduces Fehling's solution and ammoniacal silver nitrate on warming. If an alcohol solution of fisetin be acidified with sulphuric acid and treated on the water-bath with sodium amalgam, the liquid acquires a beautiful purple-red color.

When heated with glacial acetic acid and sodium acetate, fisetin yields a h e x a c e t y l - f i s e t i n, $C_{23}H_{10}(C_2H_3O)_3O_9$, which crystallizes in white needles sparingly soluble in boiling alcohol, readily in chloroform, and melting at 200° to 201° C.

When fisetin is dissolved in a warm saturated solution of sodium carbonate, a s o d i u m d e r i v a t i v e, $C_{23}H_{14}Na_2O_9$, crystallizes

out in yellow glistening needles, which turn greenish-black on exposure to air. When fused with caustic potash, fisetin yields p h l o r o g l u c o l a n d p r o t o c a t e c h u i c a c i d.

Fisetin presents a close resemblance to q u e r c e t i n, from which, if the formula of Liebermann and Hamburger for the latter be correct, it only differs by CO_2.[1]

A decoction of young fustic gives a fine orange color with alkalies, and bright orange precipitates with lime and baryta water, stannous chloride, and lead acetate. Acids give it a greenish hue. Ferric sulphate produces an olive-green, and cupric acetate a dark red precipitate.

Young fustic gives a fine orange color with alumina mordants, and is employed in conjunction with cochineal and lac-dye in dyeing scarlet, the mordants being tartar and stannous chloride. It is also used for dyeing leather orange-yellow. The colors are not so fast as many vegetable yellows and oranges.

On the fibre, colors dyed with young fustic are unchanged by hydrochloric acid, the solution becoming pale yellow. Soda and ammonia turn the fibre reddish-brown, and nitric acid dark brown. Alcohol and an acid solution of stannous chloride have no action. Heated with ferric chloride the fibre becomes olive.

WELD consists of the leaves and other parts of a variety of mignonette. *Luteolin*, the coloring matter of weld, probably has the formula $C_{20}H_{14}O_8$, and forms small yellow needles having an astringent, bitter taste. It dissolves slightly in cold and very sparingly in boiling water, but is more soluble in alcohol. It dissolves readily in alkalies with deep yellow color, and in cold sulphuric acid to form a reddish-yellow solution precipitated on dilution with water. Ferric chloride employed in small proportion produces a green coloration, which changes to brownish-red on adding excess of the reagent. Oxidizing agents, such as potassium bichromate, turn luteolin a brilliant yellow. On fusion with potash, luteolin yields h y d r o g e n, p r o t o c a t e c h u i c a c i d, and much p h l o r o g l u c o l.

A decoction of weld is pale yellow when freshly prepared, but soon becomes turbid, and gives a greenish-brown precipitate containing iron. It is slightly acid, and turns reddish when kept. Alkalies change the color to a golden yellow, and baryta water

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[1] According to H l a z i w e t z and P f o u n d l e r, the formula of quercetin is $C_{27}H_{18}O_{12}$. Herzig ascribes to it the formula $C_{15}H_{10}O_5$.

precipitates beautiful yellow flocks.   Alum gives only a slight yellow precipitate, but lead acetate and stannous chloride produce abundant yellow precipitates.   Gelatin only renders the liquid slightly turbid, while ferric sulphate gives an olive-brown coloration, and, on standing, a brown precipitate.   Chlorine changes the color of a decoction of weld to brown, and gives a flocculent precipitate; an excess of the reagent partially decolorizes the liquid.   Potassium bichromate changes the color to golden yellow, and then gives a precipitate in yellow plates.   Most acids render the liquid turbid, but nitric acid deepens the color, without producing any precipitate.

An aqueous solution of weld dyes wool, mordanted with alum, a fine daffodil-yellow, which is very fast to light, heat, and dilute acids.

On the fibre, colors dyed with weld are little affected by hydrochloric acid, though the solution is turned pale yellow.   Ammonia, alcohol, nitric acid, boiling lead acetate, and an acid solution of stannous chloride have little or no visible action.   With caustic soda the fibre is but little affected, but the solution becomes pale yellow.

PERSIAN or YELLOW BERRIES are the fruit of the buckthorn and other species of *Rhamnus* growing in the east and the south of Europe.   They are about the size of peas, shrivelled, and yellowish-green in color.   When old or injured they are brown or black. The flavor of yellow berries is bitter and disagreeable, and the odor unpleasant.

Xanthorhamnin or *Chrysorhamnin*, the yellow coloring matter of Persian berries, has, according to L i e b e r m a n n and H ö r - m a n n, the formula $C_{48}H_{66}O_{29}$.   It forms golden yellow crystals, and, when boiled with dilute sulphuric acid, or even when simply heated to 130°–160° C., it is hydrolyzed into r h a m n e t i n and the saccharoid body i s o - d u l c i t o l (see vol. i).   The following formula expresses the decomposition which is stated to occur:—

$$C_{48}H_{66}O_{29} + 5H_2O = 2C_{12}H_{10}O_5 + 4C_6H_{14}O_6$$
$$\text{Xanthorhamnin.} \qquad \text{Rhamnetin.} \qquad \text{Iso-dulcitol.}$$
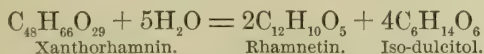
Rhamnetin crystallizes from water containing sulphuric acid in microscopic needles, and from phenol in distinct yellow needles.

A freshly prepared decoction of yellow berries has a brownish-green color.   It is very liable to ferment and become ropy, but the change may be prevented by addition of carbolic acid.   The

solution is brightened or rendered slightly turbid by acids, while alkalies change the color to orange. Alum weakens the color without forming a precipitate, and chlorine deepens it to red, or with excess changes it to yellow. Acetate of lead renders the decoction of yellow berries turbid after a time, and other metallic solutions fail to produce characteristic changes.

Persian berries give bright yellows on wool and cotton with alumina or tin mordants. Their use has much diminished.

SAFFRON consists of the stigmata of the flowers of *Crocus sativus*, of which from 50,000 to 100,000 are required to produce 1 lb. weight. It has an agreeable odor, and a bitter pungent taste.

The chemistry of saffron has been recently re-investigated by R. Kayser (*Jour. Soc. Dyers*, &c., i, 43). The essential oil is obtained by distilling saffron with water in a current of carbon dioxide, agitating the distillate with ether, and evaporating the ether in an atmosphere of carbon dioxide. It is a very mobile, nearly colorless liquid of the terpene class, $C_{10}H_{16}$, having an intense odor of saffron, and very prone to absorb oxygen and become thick and brown.

If saffron be treated with ether, to remove the fat and essential oil, and the residue treated with cold water, the coloring matter is dissolved. On shaking this solution with purified animal charcoal the color is rapidly absorbed, and on filtering and boiling the charcoal with rectified spirit, it again passes into solution. The filtered liquid yields c r o c i n on evaporation.

Crocin, so obtained, according to R. Kayser has the formula $C_{44}H_{70}O_{28}$. It forms a yellowish-brown mass, the powder of which is yellow. It dissolves readily in water and dilute alcohol, but with difficulty in absolute alcohol or ether. Concentrated sulphuric acid dissolves it with a blue color, changing to violet, cherry-red, and finally to brown. Concentrated nitric acid also gives a blue coloration, changing to brown, but hydrochloric acid dissolves crocin without alteration.

By the action of hot lime or baryta water, or even hot acetate of lead solution, crocin is hydrolyzed with formation of a g l u-c o s e, crystallizing in rhombs, and a body called c r o c e t i n, $C_{34}H_{46}O_{9}$. The latter is best prepared by heating crocin with dilute hydrochloric acid in a current of carbon dioxide, when crocetin is precipitated as a red powder, scarcely soluble in water, but soluble in presence of an alkali with orange color, and repre-cipitated on adding an acid.

Picrocrocin, $C_{28}H_{66}O_{17}$, is obtained in bitter prismatic crystals, melting at 75°, and soluble in water and alcohol, on extracting dried saffron with ether for a prolonged time. When warmed in aqueous solution with a dilute acid, lime or baryta water, or lead acetate, picrocrocin splits up into a sugar and the terpene of a saffron-odor already described.

Saffron is too expensive to use in dyeing, but is employed for coloring pastry, and has a limited use in medicine. It is liable to various substitutions and adulterations, which are classified by J. M. M a i s c h (*Analyst*, x, 200) as those derived from the same plant and those coming from other sources. The stigmata of which genuine saffron consists become thinner towards the leaves, *terminate in a yellow thread*, and three are generally united. Saffron *styles* are present in all saffron of Spanish origin to a greater or less extent, and crocus *stamens*, dyed so as to resemble the stigmata, are also met with. Fibres of shredded *beef* and *ham* are said to be a common adulterant in Italy. Such an addition would be readily detected by the microscope, and the smell produced on heating will afford a preliminary indication of their presence. The *corolla tubes* of the crocus, dyed with brazil-wood or santal-wood, are said to be frequently used for adulterating saffron. Various other colored vegetable products are referred to by Maisch, including the *calendula* florets (marigold) dyed by *dinitrocresylate of sodium* observed by J. B i e l. This fraud may be detected by treating the suspected portions of the sample with petroleum ether, which is not colored by genuine saffron, but dissolves the coal-tar color with citron-yellow color. The coloring matter from *santal-wood* is not taken up by water, but dissolves in alcohol with red and in ammonia with purple-red color. Brazil-wood will tinge the water red in a few minutes, the color becoming pale on adding acid and deeper with ammonia, but the infusion will not be blackened by salts of iron.

Safflower and *red poppy* have also been observed as adulterants of saffron. In the latter case the infusion is turned grayish-green by ammonia, and bright red by nitric acid. Safflower is said to be so commonly substituted for saffron in some parts of America that the genuine substance is unknown (*Pharm. Jour.* [3], vi, 950).

Mineral additions, such as chalk, gypsum, barium and sodium sulphate, emery, &c., have been observed as adulterants of saffron, being made to adhere by means of honey, glucose, or glycerin.

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The ash of genuine saffron of good quality ranges from 4 to 7 per cent., but in samples of Alicante saffron D. H a n b u r y (*Pharm. Jour.* [3], i, 241) found proportions of ash varying from 12 to 28 per cent., the excess being due to mineral adulterants.   J. I n g- h a m has described a sample of saffron containing 45 per cent. of mineral impurity, besides a quantity of crocus stamens; J. H a r t a saffron yielding 20 per cent. of ash, the greater part of which consisted of barium sulphate; and T a n n e r a sample containing a considerable quantity of a red ferruginous earth.   M. A d r i a n has described a saffron yielding 26.4 per cent. of ash, containing borate, chloride, sulphate of sodium, and carbonate of potassium, the last having probably been derived from tartrates.   The pres- ence of ammonium nitrate was also suspected.   E. M. H o l m e s (*Pharm. Jour.* [3], xix, 666) met with an adulterated saffron of excellent odor and color, which immediately colored water orange- yellow, deflagrated like touch-paper on ignition, gave a fusible ash, and yielded the brown coloration indicative of a nitrate with ferrous sulphate and sulphuric acid.

G r i s p o found vegetable filaments of unknown origin in saffron, together with water, glucose, and barium sulphate.   K a n o l d t examined a factitious saffron that consisted entirely of an alga, probably *Fucus amylaceus*, which had been weighted with a colored mixture of chalk and honey.

For the detection of mineral adulterants in saffron, D. H a n- b u r y recommends that about 1 grain of the sample should be treated on a watch-glass with 8 or 10 drops of water, and then lightly touched so as to cause the water to wet it.   Genuine saffron will yield immediately a *clear* bright yellow solution, but if a min- eral adulterant be present a white powder will *instantly separate*, and will render the liquid turbid; and on adding hydrochloric acid a perceptible effervescence and disappearance of the turbidity will be observed if a carbonate be present, whereas the pollen from crocus stamens is unaffected, and its nature can be recognized under the microscope.   If it be desired to collect the adulterant, the saffron should be stirred with water in a funnel closed at the lower end.   The mineral matter will settle into the stem, and after removing the saffron and pouring off the bulk of the water, can readily be washed out and further examined.

If genuine saffron be scattered on the surface of warm water, it immediately expands into a characteristic form, readily distin- guished from crocus stamens, or the florets of safflower, marigold, or arnica.

According to the *German Pharmacopœia*, "if 1 part of saffron be macerated in 10 parts of water, a yellow-red liquid is obtained free from sweet taste, and which, diluted with 10,000 parts of water, has a distinct yellow color. Saffron on being dried at 100° C. should lose less than 14 per cent. of moisture, and on being incinerated should leave not more than 8 per cent. of ash." From this description it appears that 1 grain of saffron will color 7 gallons of water distinctly yellow.

B. S. P r o c t o r (*Pharm. Jour.* [3], xix. 801) states that saffron is best assayed, in the absence of other coloring matters, by comparing the color of the infusion with that of a solution of potassium bichromate. 1.4 grammes of this salt, dissolved in 100 c.c. of water, is said to furnish a liquid of the same tint as that produced by exhausting 0.1 gramme of genuine saffron by several alternate treatments with methylated spirit and water, and diluting the mixed decoctions to 100 c.c. These solutions are too strong for the accurate observation of the color, and hence should be further largely diluted before comparing the tints. 1 c.c. of the bichromate solution should be measured with a delicate pipette, and diluted with 50 c.c. of water. To a similar quantity of water, in another tube, sufficient of the saffron infusion is gradually added from a graduated pipette to render the color similar to that of the bichromate solution.

Saffron gives a fine yellow color on silk, but is now rarely if ever used as a dye. It is employed in medicine, and would probably be more extensively applied if the price were lower.

ANNATTO, occasionally called *arnotta* and *rocou*, is mainly composed of the pulp surrounding the fruit of *Bixa orellana*, growing in the East and West Indies and South America. The two chief kinds which reach England are Spanish annatto, imported from Brazil, and the flag or French annatto which comes from Cayenne. Brazil annatto occurs in cakes or rolls, is hard and dry, brownish on the exterior but red inside, and with a rather agreeable odor. Cayenne annatto is a soft paste, of a bright yellow color. It often has a repulsive urine-like odor, said to be due to the actual addition of urine to keep it moist and impart a richer color.

Annatto contains two yellow coloring matters, b i x i n and o r e l l i n.

Bixin, $C_{28}H_{34}O_5$, the properties and chemical relationships of which have been very imperfectly examined, may be prepared by digesting annatto at about 80° C. with rectified spirit and sodium

carbonate. The filtered liquid is treated with half its measure of water and a saturated solution of sodium carbonate. The precipitate, consisting of the sodium salt of bixin, is purified by resolution in weak alcohol and precipitation by sodium carbonate, and is then decomposed by hydrochloric acid. Bixin forms minute yellow leaflets which melt at 176°. It is insoluble in water, and only slightly soluble in alcohol, benzene, carbon disulphide, or acetic acid, but is very readily soluble in ether.[1] Bixin forms a s o d i u m s a l t, containing $C_{28}H_{33}NaO_5$, 2 H_2O, which crystallizes in lustrous red needles, very soluble in water, but insoluble in alcohol and ether. It also yields a compound containing $C_{28}H_{33}Na_2O_5$, 2 *aqua*, which forms a dull red powder.

According to some observers, bixin reduces Fehling's solution even in the cold, but according to others it has no action even after boiling with dilute sulphuric acid. It dissolves in strong sulphuric acid with bright blue color, and on dilution with water a dark green precipitate is formed.

Orellin is described as yellow, soluble in water and alcohol, but insoluble in ether, and dyeing cloth mordanted with alum yellow. It is probably an oxidation-product of bixin.

Annatto is only partially soluble in water, but more completely in alcohol. It dissolves readily but sometimes imperfectly in solutions of caustic and carbonated alkalies, of borax, and of soap, forming liquids of orange or red color, which furnish orange-red precipitates with acids. It gives orange lakes with alumina and ferrous sulphate, a yellowish-brown precipitate with salts of copper, and a lemon-yellow with tin salts. Concentrated sulphuric acid dissolves annatto with deep blue color, the color gradually changing to green and violet. On adding water a deep green precipitate is formed.

Commercial annatto varies greatly in quality, and is liable to various adulterations. According to W y n t e r B l y t h, a fair commercial sample contained:—water, 24.2; resin, 28.8; ash, 22.5; and extractive matters, 24.5 per cent. An adulterated sample contained:—water, 13.4; resin, 11.0; ash (oxide of iron, alumina, silica, chalk, and common salt), 48.3; and extractive matters, 27.3 per cent. C r a c e - C a l v e r t gives the average composition of inferior Cayenne annatto as:—water, 72.25; leaves, 3.85; starch, mucilage, and woody fibre, 18.30; and, coloring matter, 5.60 per cent.

[1] According to some authorities, bixin is insoluble in ether, but readily soluble in alcohol.

The following results, obtained by the analysis of commercial annatto, have been recorded by W. L a w s o n (*Pharm. Jour.* [3], xvi, 645).

No of Sample.	Mois-ture.	Resin.	Extrac-tive.	Total Ash.	Soluble Ash.	Remarks.
1	21.75	3.00	57.29	17.96	13.20	Red roll. Ash was largely NaCl.
2	21.60	2.90	59.33	16.17	12.57	Red roll. Ash was largely NaCl.
3	20.39	1.00	65.00	13.61	7.50	Red roll. Ash large, chiefly NaCl and Fe_2O_3.
4	69.73	8.80	19.47	2.00	. .	Bright red paste. Ash chiefly NaCl.
5	18.00	3.00	58.40	20.60	10.00	Red roll. 3 per cent. of sand.
6	18.28	1.80	65.67	14.25	11.75	Red roll. Contained iron and foreign matters.
7	15.71	5.40	26.89	52.00	18.50	Brown cake. Soluble ash chiefly K_2CO_3, and insoluble $CaCO_3$.
8	38.18	1.20	20.82	29.00	20.00	Brown cake. Very offensive. Soluble ash chiefly K_2CO_3.
9	19.33	5.99	23.77	51.00	15.00	Brown cake. Resembled No. 7.
10	29.50	9.20	28.50	39.80	13.80	Brown cake. Resembled No. 7.

The *resin* was determined by drying the samples at 100° (the loss of weight being recorded as *moisture*), and then exhausting with boiling methylated spirit. The alcoholic solution was evaporated on the water-bath, the residue dissolved in carbonate of sodium, and the solution precipitated by a very slight excess of dilute sulphuric acid. The precipitated resin was filtered off, washed, dried, and weighed. The *ash* was determined by ignition, and the *extractive matter* by difference.

The samples in the form of brown cakes gave on ignition an agreeable odor resembling that of good tobacco. Most of the red rolls contained abundance of starchy matters, this in No. 4 being largely replaced by water. The cakes all gave the boric acid reaction for turmeric, and all except No. 8 contained large quantities of chalk.

Besides containing the adulterants already mentioned, annatto is liable to be mixed with ochre, brick-dust, &c.

The coloring power of annatto is best ascertained by a dye-assay in a bath containing soap or sodium carbonate.

Annatto receives a limited application in dyeing and calico-printing, but by far the greater part is employed for coloring butter and cheese.

Butter colorings are now numerous. Among the substances employed for the purpose, E. S c h m i d t (*Jour. Chem. Soc.*, xlvi, 286) enumerates marigold and carthamus flowers, saffron (?), carrot juice, and turmeric. More recently the coal-tar colors known as coralline yellow and Victoria yellow are said to have been used, as also dimethyl-amido-azobenzene. Lead chromate has been met with as a color on the outside of cheese.

Various methods have been described for the recognition of butter-colorings, the process being usually based on the solution of the butter-fat in ether or similar solvents, the agitation of this liquid with alkali, the precipitation of the dissolved coloring matter by an acid, and the application of special tests to the precipitate.

To extract *naphthalene-yellow* from butter, the fat should be separated from the curd, water, &c., dissolved in ether, and the solution agitated with water, to which dilute ammonia is added drop by drop until present in slight excess. The naphthalene yellow or other added coloring matter, *e. g.*, annatto, turmeric, saffron, &c., will dissolve in the ammoniacal liquid. *Turmeric* will be indicated by the formation of a brownish or reddish stratum between the ethereal and aqueous layers before they are thoroughly mixed by agitation.

E. W. M a r t i n (*Analyst*, xii, 70) recommends that 2 parts of carbon disulphide should be gradually added, with gentle agitation, to 15 parts of alcohol or wood spirit. Five grammes of the butter to be tested, which need not be previously clarified, is shaken with 25 c.c. of the solution so obtained. On standing for a few minutes, the mixture separates into two layers, the lower of which is a solution of the fat in carbon disulphide, while the upper alcoholic stratum will be yellow if any artificial coloring matter be present. If the butter be but slightly colored, a larger amount should be employed. The alcoholic stratum will give a greenish coloration with nitric acid, and a red with hydrochloric acid and sugar if *saffron* be present. A brownish color with ammonia indicates *turmeric*, and a blackish coloration with silver nitrate, *marigold*. If the alcoholic solution be evaporated to dryness, and the residue treated with concentrated sulphuric acid, *annatto* will be indicated by a greenish-blue, and *saffron* by a blue coloration. On adding a few drops of boric acid solution (or a solution of borax to which sufficient hydrochloric acid has been added to distinctly redden litmus), and again evaporating, *turmeric* will be

indicated by a bright brownish-red coloration, changed to blue, green, or violet by caustic alkalies. *Dinitro-cresol* and *dinitro-naphthol* will be detected by treating the residue with ammonia, and adding excess of hydrochloric acid, when a light yellow crystalline precipitate will be 'formed, soluble in ether. The residue obtained, on evaporating the ethereal solution, is soluble in alcohol, and after dilution with water the hot solution will dye a fibre of silk or wool yellow without a mordant.

R. W. M o o r e has pointed out (*Analyst*, xi. 163) that, when a butter colored with *carotin* is dissolved in carbon disulphide and shaken with alcohol, as prescribed by Martin, the alcohol remains colorless, while the lower layer is deeply colored; but on adding a drop of a dilute solution of ferric chloride and again shaking, a gradual change is observed, the alcoholic layer becoming distinctly yellow and the bisulphide solution of the fats quite colorless, or retaining only the pale yellow color due to the natural coloring matter of the butter. Excess of ferric chloride must be avoided.

A. R. L e e d s (*Analyst*, xii. 150) has described a general method for the detection of butter-colorings. He recommends that 100 grammes of the butter should be dissolved in a tapped separator in 300 c.c. of petroleum ether of about 0.638 specific gravity. The water, etc., are tapped off, and ethereal solution of the fat and coloring matters washed several times by agitation with water. The ethereal solution, poured off from any stearin which may have separated on standing, is then shaken with 50 c.c. of a decinormal solution of caustic potash (5.61 grammes of KHO per litre), which is usually sufficient to effect the solution of all coloring matters capable of being dissolved by dilute alkali.[1] The alkaline solution is separated from the ethereal layer, and very cautiously treated with dilute hydrochloric acid until faintly acid to litmus paper. The precipitate, consisting of coloring matter mixed with a little fatty acid, is filtered off and washed with cold water. If desired, it may be weighed.

The following table shows the reactions of the coloring matters, isolated in the above manner, when two or three drops of their alcoholic solutions were treated with an equal measure of the reagents (acids) mentioned.

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[1] Even after agitation with caustic alkali the petroleum ether always retains a pale yellow color, which is not removed or lessened by repeating the treatment with alkali. This is due to the natural or yellowish color of the butter fat itself, and not to any added coloring matters. It may be destroyed without any sensible change to the butter fat.

COLORING MATTERS.	REACTION WITH			
	CONCENTRATED SULPHURIC ACID.	CONCENTRATED NITRIC ACID.	MIXED SULPHURIC AND NITRIC ACIDS.	CONCENTRATED HYDROCHLORIC ACID.
Annatto.	Indigo-blue, changing to violet.	Blue, becoming colorless on standing.	Blue, becoming colorless on standing.	No change, or merely dirty yellow or brown color.
Annatto with decolorized butter.	Blue, becoming green and slowly changing to violet.	Blue, becoming green and colorless.	Decolorized.	No change, or only dirty yellow.
Turmeric.	Rose-violet.	Violet.	Violet.	Violet, becoming yellow on evaporation of the acid.
Turmeric with decolorized butter.	Violet, changing to purple.	Violet to reddish-violet.	Violet to reddish-violet.	Very fine violet.
Saffron.	Violet to cobalt blue, changing to reddish-brown.	Light blue, changing to light reddish-brown.	Light blue, changing to light reddish-brown.	Yellow, changing to dirty yellow.
Saffron with decolorized butter.	Dark blue, rapidly changing to reddish-brown.	Blue, changing to green and brown.	Blue, rapidly changing to purple.	Yellow, becoming dirty yellow.
Carrot.	Amber brown.	Decolorized.	Decolorized, with red fumes and odor of burnt sugar.	No change.
Carrot with decolorized butter.	Reddish-brown to purple.	Yellow and decolorized.	Yellow and decolorized.	Slightly brown.
Marigold.	Dark olive green, not changing in color.	Blue, instantly changing to a dirty yellowish-green.	Green.	Green to yellowish-green.
Safflower.	Light brown.	Partially decolorized.	Decolorized.	No change.
Aniline yellow.	Yellow.	Yellow.	Yellow.	Yellow.
Martius yellow.	Pale yellow.	Yellow-red precipitate; magenta at margin.	Yellow.	Yellow precipitate, which deflagrates when treated with ammonia and heated.
Victoria yellow.	Partially decolorized.	Partially decolorized.	Partially decolorized.	Yellow color returns on neutralizing with ammonia.

The butter-coloring sold as "carottine" is apparently a solution of 1 part of annatto in 4 parts of oil, the annatto being partially replaced by turmeric for the lighter shades. "Orantia" is a solution of annatto and carbonate of sodium in water.

CAROTIN, the coloring matter contained in the root of the carrot (*Daucus carota*), may be prepared by exhausting the finely-divided root with water, precipitating the solution with tannin and a little sulphuric acid, and exhausting the washed precipitate with boiling alcohol at 80 per cent. This takes up m a n n i t o l, $C_6H_{14}O_6$, and h y d r o c a r o t i n, a body closely resembling c h o l e s t e r i n. The residue insoluble in alcohol is treated with carbon disulphide, the resultant solution evaporated, and the residue treated with absolute alcohol. The solution obtained yields, on concentration, a precipitate of carotin as a brownish-red crystalline substance with a metallic reflection. Pure carotin forms rhombic leaflets, which appear blue in reflected and red-orange in transmitted light. It is soluble in benzene and carbon disulphide, but insoluble in water or hydrous alcohol. Carotin is decolorized by heat or exposure to light. It dissolves in sulphuric acid with an indigo-blue or violet color, while sulphurous acid also colors it indigo-blue. With iodine it yields a derivative of a deep green color and metallic lustre.

H u s e m a n n attributed to carotin the formula $C_{18}H_{24}O$, but according to A r n a u d this was probably an oxidized product, the pure substance being an unsaturated hydrocarbon of the formula, $C_{28}H_{28}$, which he proposed to call c a r o t e n e. This latter formula is probably incorrect, as no other colored hydro-carbon is known.

Carotin appears to be a constant and normal product of vegetable life, and to be frequently present in the leaves of the most vigorous plants, and consequently those that are the most intensely green, its presence in such cases being masked by the green color of the chlorophyll. It may be detected and approximately estimated by carefully drying the leaves in a vacuum over sulphuric acid, digesting in the cold for ten days with petroleum spirit, evaporating to dryness in an open dish, and dissolving the residue in a little carbon disulphide. The resultant solution is intensely red, and is examined colorimetrically against a standard solution of pure crystallized carotin, containing 0.010 gramme per litre. The proportion of carotin in dry leaves often approaches 0.1 per cent.[1] (M. A. A r n a u d, *Jour. Soc. Dyers, &c.*, iii. 99.)

[1] O. H e s s e (*Annalen*, cclxxi. 229) considers this method as unreliable, especially as rubidin, another red coloring matter has been shown by N e g r i to exist in various plants.

Turmeric or INDIAN SAFFRON is the tuber or underground stem of *Curcuma tinctoria* or *longa* and *C. rotunda*. The color of the roots externally is generally grayish, but in the interior they are usually a deep yellow.[1]

According to J o h n, turmeric-root contains:—yellowish volatile oil, 1; yellowish-brown resin, 10 to 11; brown extractive matter, with dyeing properties, 11 to 12; gummy matter, 14; matter soluble in alkalies, including earthy salts, 57; and moisture, loss, etc., 7 to 5 per cent. The presence of starch is not indicated in this analysis, though turmeric-root contains a sufficient proportion for iodine solution to change the whole color from yellow to blue.

The powder of turmeric has a strong odor and a very bright orange color. The taste is bitter and aromatic. Cold water dissolves but little coloring matter, but boiling water extracts a larger quantity. Alcohol dissolves the coloring matter freely, and likewise takes up the greater part of the resin.

Curcumin, $C_{14}H_{14}O_4$,[2] is prepared by F. W. D a u b e by steaming powdered turmeric to remove the volatile oil, washing with boiling water till the washings are no longer colored, drying, and extracting the residue with a large quantity of boiling benzene. The solution is evaporated to the crystallizing point, the crystals dissolved in spirit, the solution precipitated with basic lead acetate, and the lead compound decomposed by sulphuretted hydrogen. The product is recrystallized from boiling alcohol. Another method is to exhaust ground tumeric with carbon disulphide to remove the volatile oil and resinous matters, and treat the residue with weak caustic alkali. On neutralizing the alkaline solution with an acid, the curcumin is precipitated, and after drying may be recrystallized from ether.

According to J a c k s o n and M e n k e (*Amer. Chem. Jour.*, iv.

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[1] The principal commercial varieties of turmeric are:—*Chinese*, consisting of many central rhizomes with well-developed branches; *Bengal*, mostly in slender branches of a deep reddish tint; *Java*, which consists of rather small tubers and branches that are often transversely and longitudinally cut; and *Cochin turmeric*, in sections or slices of a larger tuber, some being marked with rather large depressed stem-scars.

[2] The following structural formula has been assigned to this substance :

$$C_6H_3 \begin{cases} (1)CH < ^{C_5H_5}_{COOH} \\ (3)O.CH_3 \\ (4)OH. \end{cases}$$
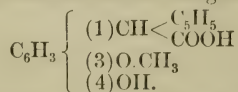
Ciamician and Silber (*Ber.*, xxx. 192) adopt the formula of $C_{19}H_{14}O_4$-$(OCH_3)_2$ as correct for curcumin.

77, and *Jour. Chem. Soc.*, xlii. 1107) curcumin may be obtained pure by treating ground turmeric-root with petroleum spirit to remove the volatile oil, and then with ether, which dissolves the curcumin together with a large quantity of resin. The product is purified by crystallization from alcohol. Thus prepared, curcumin crystallizes from hot alcohol in stout needles or shining prisms, which have an orange or red color and a beautiful blue reflection. Curcumin is odorless when pure, melts at 178° C., and is only slightly soluble in water, even when boiling. It is difficultly soluble in cold but more readily in boiling alcohol, and is also soluble in ether, the solution exhibiting a strong green fluorescence. It is also soluble in wood spirit and glacial acetic acid, but only slightly so in benzene or carbon disulphide, and is all but insoluble in petroleum spirit. Strong sulphuric acid dissolves curcumin with a fine reddish-purple color, gradually changing to black from charring, and the same effect is produced, though more slowly, by strong hydrochloric acid.

Curcumin dissolves readily with a reddish-brown color in solutions of caustic and carbonated alkalies, and to a slight extent when boiled with water and calcium carbonate. The ammoniacal solution gives off ammonia when boiled, and deposits curcumin. On adding a large excess of strong alcoholic potash to a hot alcoholic solution of curcumin, the p o t a s s i u m   s a l t, $C_{14}H_{12}K_2O_4$, separates in globular radiated groups of flame-colored crystals, which assume a claret color when dried. The precipitation may be made more perfect by adding ether, in which the new compound is nearly insoluble, though soluble in alcohol and freely so in water. On exposure to air, the alcoholic solution of potassium curcumate assumes a magenta color, probably from oxidation. When excess of potassium carbonate is added to a hot solution of curcumin in absolute alcohol, the a c i d   s a l t, $C_{14}H_{13}KO_4$, is formed, and on adding ether separates in crimson-black flocks resembling magenta. The solution gives colored precipitates with metallic salts.

By treatment with chromic acid mixture curcumin is completely oxidized to acetic and carbonic acids, without any terephthalic acid being formed. By oxidation with permanganate in alkaline solution it yields v a n i l l i n.

In consequence of the sensitiveness of curcumin to alkalies, turmeric is sometimes used as an indicator of alkalinity. The yellow color is restored by very weak acids, and hence turmeric has been

proposed for titrating fatty acids, for which purpose, however, phenol-phthaleïn is better adapted (see vol. ii.; and R. T. Thomson, *Jour. Soc. Chem. Ind.*, vi, 195).[1] The alcoholic solution of turmeric exhibits a well-marked fluorescence.

The most characteristic reaction of curcumin and turmeric is that with boric acid. If an alcoholic solution of turmeric or curcumin be mixed with one of boric acid, it becomes a deep red color, distinct from that produced by alkalies. A convenient way of applying the test is to place a small disk of filter-paper, about 1 inch in diameter, in the turmeric tincture, and evaporate the latter to dryness at 100°. On the paper is then poured an aqueous solution of boric acid, or a solution of borax to which sufficient hydrochloric acid has been added to render it distinctly acid to litmus. The red color will probably be at once developed, but if not will become apparent on evaporating the liquid to dryness. On now adding a drop of caustic alkali, a very beautiful series of colors will be produced, green and purple being the most prominent.[2] On adding hydrochloric acid a red color is produced which is again turned green and blue on addition of excess of alkali.

The reaction of curcumin with boric acid appears to be due to the formation of a substance called by S c h l u m b e r g e r r o s o-c y a n i n, which may be prepared by treating an alcoholic solution of curcumin with boric and sulphuric acids. The liquid acquires a deep red color, which changes gradually in the cold, and rapidly on heating, to dark red, orange, and finally to yellow. Hence the operation should be arrested when a sample is found to become blue on adding ammonia. The impure rosocyanin crystallizes out as the solution cools. When pure, it forms dark red needles with a green reflection, and is insoluble in water, ether, or benzene. The alcoholic solution has an intense rose-red color, but rapidly changes. It is turned blue by ammonia, the original color returning on adding an acid. The alkaline solution becomes gray on exposure to air, and gives blue precipitates with lime or baryta water.

Turmeric is not employed alone as a dye for fabrics (except in China), but is used to some extent in certain mixed colors known as "sour browns." It is one of the few coloring matters for which

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[1] Turmeric is also applicable in the presence of ammonia, to which it is not sensitive.

[2] In 1874, the author recommended this mode of operating to effect the detection of turmeric in mustard (*Chem. News*, xxx, 116).

cotton has a strong attraction. Cotton may be dyed without a mordant by heating in a bath of turmeric at 60°. Turmeric is also employed in paper-staining, and for dyeing wood and leather; also as a coloring for butter, cheese, pastry, etc. It is an important ingredient of curry powder.

Powdered turmeric is sometimes adulterated with starch and mineral matters. The *ash* should not exceed 5 to 6 per cent. Common salt is added to turmeric to give it a brighter appearance, but interferes with some of its uses. Turmeric should be quite dry. If damp it becomes yellowish-brown, and is rendered unfit for its chief applications. The characteristics of good turmeric are a rich, deep, but bright, orange color, and a strong aromatic, rather pungent odor. Turmeric may be assayed by dyeing equal weights of white woolen cloth at 60° C. with solutions of equal weights of the samples, using no mordant. The dyed pieces are examined for depth of color, and also held horizontally in front of a window and viewed along the surface. In this position cloth dyed with good turmeric shows a beautiful golden lustre, on the purity of which its value for many purposes depends, as for the yellow cotton warps of figured table-covers.

On the fibre, turmeric is turned reddish-brown by hydrochloric acid, or an acid solution of stannous chloride, without the solution becoming colored. Caustic soda and ammonia turn the fibre bright reddish-brown, the solution becoming brownish-orange. Alcohol extracts the color, producing an orange or yellow solution with green fluorescence. Nitric acid turns the fibre pale yellow.

Gamboge is a gum-resin produced by trees growing in various parts of the Malay peninsula. It occurs in cylindrical, hollow, or solid rolls,[1] longitudinally striated on the surface, and either distinct or more or less agglutinated or folded together in masses. Externally it is brownish-yellow, and is covered with a yellow powder. When broken it exhibits a vitreous or conchoidal fracture, the fractured surface being opaque, smooth, glistening, and of a uniform reddish-yellow color. The powder is bright yellow, and forms a yellow emulsion with water. Although nearly without odor at the ordinary temperature, gamboge evolves a very peculiar smell when heated. The taste is at first scarcely per-

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[1] The cylindrical variety of gamboge is produced by running the juice into bamboo-canes. On drying, the gamboge contracts, and consequently holes are often seen through the middle of the cylinders. Inferior gamboge often occurs in irregular masses weighing several pounds.

ceptible, but after a time it produces a sharp acrid sensation in the throat. Gamboge acts as a drastic purgative, and is the active constituent of a well-known patent pill.

Gambogin or *Gambogic Acid,* the resin of gamboge, according to B u c h n e r has the formula $C_{30}H_{35}O_6$. It may be obtained by precipitating the filtered alcoholic solution of gamboge by water, treating the dried precipitate with ether, and evaporating the ethereal solution. It may be obtained less pure by treating the original gamboge with ether. Gamboge is a transparent, vitreous brittle resin, breaking with a conchoidal fracture. The color is hyacinth- or orange-red, and the powder bright yellow. It softens on heating and melts at 75°–80° C., solidifying to a glassy mass on cooling. It is tasteless, and, according to Hurst, has no purgative action. Gamboge-resin is readily soluble in alcohol, ether, and chloroform, but is only slightly soluble in petroleum spirit. Gambogin has well-marked acid properties, decomposing carbonates of the alkali-metals at a boiling heat. It dissolves in caustic alkalies with orange-red color, and is precipitated in gelatinous flakes on acidulating the solution. On adding excess of common salt to the solution of gambogin in caustic soda, the s o d i u m s a l t is thrown down as a red precipitate.

The *wax,* the portion of gamboge insoluble in ether but dissolved by alcohol, is described by H u r s t as a soft brownish substance, melting readily and having slight bitter taste, and persistent bitter after-taste, with slight purgative action. It is soluble in caustic soda with brownish-yellow color, being reprecipitated on adding an acid.

The *gum* of gamboge, according to G. H. Hurst, is a transparent, brownish mass, having a sweetish taste and slightly adhesive properties. It is soluble in water to form an opalescent solution, rendered clear by acids, and which is not precipitated by basic lead acetate, ferric chloride, mercuric chloride, borax, or alcohol. It appears to be a glucoside.

Gamboge dissolves in alcohol, in ether, and in ammonia. The ammoniacal solution produces a red precipitate with salts of barium, yellow with those of zinc, reddish-yellow with lead acetate, and brownish-yellow with silver nitrate.

The following analyses by C h r i s t i s o n indicate the composition of commercial gamboge:—

	PIPE GAMBOGE FROM SIAM.		CAKE GAMBOGE FROM SIAM.		CEYLON GAMBOGE.			
Resin, ...	74.2	71.6	64.3	65.0	68.8	71.5	72.9	75.5
Gum, ...	21.8	24.0	20.7	19.7	20.7	18.8	19.4	18.4
Amylaceous matter, .	. .	. .	6.2	5.0	. .	. .	. .	. .
Woody fibre, ...	. .	. .	4.4	6.2	6.8	5.7	4.3	0.6
Moisture, ...	4.8	4.8	4.0	4.6	4.6	. .	. .	4.8
	100.8	100.4	99.6	100.5	100.9	96.0	96.6	99.3

A sample of gamboge recently analyzed by G. H. Hurst (*Pharm. Jour.* [3], xix, 761) contained:—moisture, 2.50; mineral matter, 1.05; resin, soluble in ether, 66.05; wax, soluble in alcohol, 4.31; and gum, 26.03 per cent.; total, 99.94.

Commercial gamboge is liable to adulteration with *mineral matters* and *starch*. The *ash* should not much exceed 1 per cent. Starch may be detected by exhausting with alcohol, boiling the residue with water, and adding iodine to the cooled liquid, when the well-known blue coloration will be produced if starch be present. An emulsion, made by boiling the powdered sample with water, gives, after cooling, a green coloration with iodine in the presence of starch. It will be observed that the analyses of Christison of cake gamboge from Siam show a small proportion of starch.

Gamboge is not employed as a dye. It has a limited use in medicine as a purgative, and is employed as a yellow pigment in water-color painting.

Dyes of Animal Origin.

The coloring matters contained in the blood, bile, and urine receive no practical application, and, so far as they require description, will be more conveniently considered in the sequel. Exclusive of coloring matters, such as *murexide* and *prussian blue*, which are prepared by complex chemical reactions from substances originally obtained from animals, the only dyes of animal origin which require description are *cochineal*, *lac-dye*, and *kermes*. These are derived from three distinct species of a peculiar tribe of insects called *Coccina*.

Cochineal is the female of the *Coccus cacti*, an insect which lives and propagates on certain kinds of cacti, especially the nopel, or *Cactus opuntia*, a plant which grows wild in Mexico, though the insects collected from the cultivated plant are the

superior. The weight of the dried insect is about 0.1 grain, and hence 70,000 are required to produce 1 lb. of cochineal. The two chief varieties of cochineal are the white or *silver grain*, and the *black grain*. A third inferior variety, called the *granilla*, consists of very small insects, probably unimpregnated females. The silver grain, which is the finest kind of cochineal, probably consists of young females after impregnation, and the black grain of the mothers after the eggs have been laid. According to other descriptions, the color of the grains depends on the method employed for killing and drying the insects (see *Jour. Soc. Chem. Ind.*, i. 181).

Carminic Acid, $C_{17}H_{18}O_{10}$, the color-principle of cochineal, is prepared by S c h ü t z e n b e r g e r by washing the cochineal grains (insects) with ether, to remove fat, and then treating them several times with warm water. On treating the filtered liquid with a slightly acid solution of lead acetate, the whole of the coloring matter is thrown down as a violet-blue precipitate. The concentrated filtrate deposits crystals of t y r o s i n e, while the precipitate consists of carminate and phosphate of lead, with a little nitrogenous matter. This is removed by thorough washing with water, and the purified precipitate is suspended with warm water and treated with barely sufficient sulphuric acid to decompose the lead carminate, leaving the phosphate unattacked. The solution of the carminic acid thus obtained is evaporated to dryness at a temperature not exceeding 40°–50° C., and residue dissolved in absolute alcohol, which on evaporation and cooling yields the carminic acid in crystals. It may be further purified by dissolving it in water, filtering, evaporating, and recrystallizing the residue from absolute alcohol or ether.

Carminic acid is a purple substance soluble in water, alcohol, carbon disulphide and benzene, and slightly soluble in ether. It does not melt or decompose at 135° C., and dissolves without decomposition in strong sulphuric and hydrochloric acids. Chlorine, bromine, and iodine readily destroy carminic acid, and nascent hydrogen reduces it to a leuco-body, which again becomes red on exposure to air.

The formula of carminic acid, according to Schützenberger, is $C_9H_8O_5$, but H l a s i w e t z and G r a b o w s k i obtained potassium and barium salts corresponding to $C_{17}H_{18}O_{10}$, and found that when boiled with dilute acids carminic acid was split up into a sugar and c a r m i n e - r e d, a purple-red substance, which appears

green by reflected light, and is cinnabar-red in powder. It is insoluble in ether, but soluble in water and alcohol with red color.[1]

Carminic acid dissolves in caustic alkalies with beautiful red color.[2] Sodium carminate crystallizes in purple plates. An aqueous solution of carminic acid gives purple precipitates with baryta and lime water, barium chloride, lead acetate, and cupric acetate; with stannic chloride, a red precipitate; and with potassium oxalate or acid tartrate, an orange-red precipitate. Alumina removes the whole of the coloring matter from an aqueous solution of carminic acid, yielding a fine red lake, which when heated becomes crimson and purple. The addition of aluminium acetate or a little acid to the lake produces the same change of color.

A decoction of cochineal behaves with reagents somewhat differently from a solution of pure carminic acid, owing to the presence of phosphates, tyrosine, etc. Acids produce a slight precipitate, and change the color to a yellowish-red, while alkalies change it to violet. Lime-water, salts of copper, lead and zinc, and stannous chloride free from excess of acid give violet precipitates, while stannic chloride give a scarlet coloration. Ferrous sulphate produces a violet-gray coloration and precipitate, and ferric acetate a brown precipitate, changing to olive-green. Alum changes the color of a solution of cochineal to red, a precipitate being also formed; while aluminium chloride produces a reddish-violet precipitate, the supernatant liquor becoming crimson.

By heating carminic acid or carmine to 200° C. with water or dilute hydrochloric acid, or to 140° with strong sulphuric acid, an insoluble red body called r u f i c a r m i n e or r u f i c o c c i n is formed.

Cochineal is somewhat liable to adulteration. A fraud said to

[1] M i l l e r and R o h d e have corrected the formula for carminic acid to $C_{11}H_{12}O_6$, or structurally:

$$CH_3 \ (OH)_2$$
$$OH$$
$$HO$$
$$(OH)_2$$
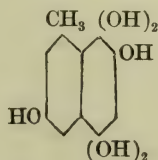
[2] Carminic acid is at times useful as an indicator; it is more sensitive to the bicarbonates of the alkaline earths than litmus. According to D r a p e r it gives a reaction with alkalies in solutions of 1 : 1,400,000. It has also been recommended as a precipitant for albumins and proteoses, it being claimed that 1 part of albumin in 90,000 parts of solution is readily detected.

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be commonly practised at certain places consists in removing part of the coloring matter by a short immersion in water. After re-drying, the partially exhausted material is sold as "black cochineal," or faced by agitation with talc, sulphate of barium, or sulphate of lead, and sold as "white cochineal." On powdering such a sample and treating it with water, the mineral adulterant will fall to the bottom of the liquid. Black iron sand, to the amount of $12\frac{1}{2}$ per cent., has been recorded as an adulterant of black Teneriffe cochineal (*Jour. Soc. Chem. Ind.*, i, 144); and graphite and black oxide of manganese are other probable adulterants. According to L o e w e, genuine cochineal leaves only 0.5 to 0.6 per cent. of ash on ignition.

In other cases the cochineal is subjected to an atmosphere of dry steam, and when the grains have swollen and become damp from the exudation of an adhesive juice they are rotated in a drum with the mineral adulterant, of which they take up from 10 to 12 per cent. On re-drying, the grains shrink up and assume their original appearance (L o e w e, *Pharm. Jour.* [3], xiii. 590).

The specific gravity of cochineal is a useful preliminary test of quality. Heavy samples are always inferior or adulterated. Partially exhausted cochineal is always deeply wrinkled, and does not, when treated with water, take up moisture equally, so that some of the insects or "grains" float, and others become only partly submerged.

To detect cochineal in alimentary substances, E. L a g o r c e recommends that the substance should be dissolved in water or weak alcohol rendered faintly acid with acetic acid. The liquid is then agitated with amylic alcohol, which is separated and evaporated in presence of water. The aqueous solution obtained is treated with a few drops of a 3 per cent. solution of uranium acetate, when a beautiful bluish-green coloration or precipitate will be produced if cochineal be present. Acids destroy this color, with production of the orange tint of the carminic acid. In the case of wine, the amylic alcohol employed should be mixed with an equal measure of benzene, or, preferably, toluene, as otherwise œnolin will also be taken up, and will mask the reaction of the cochineal. Ammoniacal cochineal, which has been occasionally employed to color wine, produces a rose-violet or violet-blue lake with uranium oxide. Logwood gives a somewhat similar reaction, but may be distinguished from cochineal by other means.

Cochineal has been occasionally adulterated with an extract of

brazil-wood. This may be detected by treating the decoction with excess of lime-water, which completely precipitates the coloring matter of cochineal, while if brazil-wood be present the filtered liquid will have a purple or violet color. Brazil-wood may also be detected by soaking cotton in the decoction and then immersing it in a warm solution of potassium bichromate, when the tissue will assume rather a deep color if brazil-wood be present.

The assay of cochineal may be effected by boiling 1 gramme of the powdered sample for an hour with 1 litre of water and 20 drops of a saturated solution of alum. After cooling, the liquid is again made up to 1 litre, and the color compared with that of a standard specimen similarly treated.

C. Lieberman (*Jour. Soc. Dyers, &c.*, i. 269) recommends that the cochineal should be exhausted as completely as possible with boiling water, and then precipitated with a slightly acid solution of lead acetate. The precipitate is washed with warm water, dried, and weighed, and the lead determined in an aliquot part of it. By deducting the amount of oxide of lead in the precipitate from the weight of the latter, that of the coloring matter is found. This method is open to the objection that phosphoric acid and other matters are estimated as carminic acid. Hence a more accurate result would be obtained by simply igniting the impure carminate of lead, and deducting the weight of the residue from that of the original precipitate. A still better determination of the coloring matter might probably be obtained by treating the moist lead precipitate with a slight excess of dilute sulphuric acid, filtering from the sulphate of lead, rendering the filtrate strongly alkaline with caustic soda, and running in a standard solution of potassium ferricyanide until the purple color of the solution changes to a dull reddish-brown. The use of ferricyanide in alkaline solution for the assay of cochineal was suggested by Penny; but when the original decoction is operated on, as proposed by him, the results are not satisfactory.

Cochineal may also be assayed by a miniature dye-test. A suitable bath may be prepared from 1 gramme of finely powdered cochineal, 1 gramme of cream of tartar, $1\frac{1}{2}$ gramme of alum, and 1 litre of water. 7 grammes of flannel should first be immersed and dyed to a full tone, and a second piece of the same weight then introduced, and allowed to remain till the bath is exhausted.

Cochineal is not used in cotton-dyeing. In dyeing silk it has also been almost entirely superseded by aniline-reds, and in wool-

dyeing the azo-colors have to a great extent replaced it; though many dyers prefer to use cochineal or alizarin colors for all scarlets, since these dyes do not bleed and stain the neighboring fibres like the azo-reds. Two distinct red shades are obtained with cochineal, according to the mordant used. *Cochineal crimson* is mordanted with cream of tartar and alum, with or without tin salts; while *cochineal scarlet* is mordanted with stannous chloride and cream of tartar or oxalic acid. Cochineal reds on wool are fairly fast to light, but become dull or bluish by the action of weak alkalies or soap, though the bright tone may be restored by immersing the fabric in water acidulated with acetic acid. A good purple color can be obtained by dyeing wool mordanted with 2 per cent. of potassium bichromate in a slightly acid cochineal bath.

Fibres dyed with cochineal are turned orange-red by hydrochloric acid, the liquid becoming pink. Sulphuric acid turns both fibre and solution a bright pink. Caustic soda and ammonia give a purple solution. Alcohol has no action, and an acid solution of stannous chloride behaves much like hydrochloric acid alone.

Cochineal is also a valuable indicator, it being violet toward alkalies and orange toward acids. It is especially serviceable for indicating the carbonates of the alkaline earths for which litmus is inapplicable; it is also useful for titrating the ammonia or the excess of sulphuric acid in the Kjeldahl method for determining nitrogen, in which phenolphthalein is not very useful.

Ammoniacal cochineal is prepared by leaving ground cochineal in contact with excess of ammonia, when a chemical action occurs which results, according to Schützenberger, in the formation of an amido-compound called c a r m i n a m i d e. After several weeks the mixture is heated to drive off part of the ammonia, and is sent into commerce in the form of a thick paste. Instead of heating the product directly, it is sometimes mixed with about 40 per cent. of hydrated alumina, and the whole then heated till no odor of ammonia can be observed. When cold the mass is moulded into cakes.

Ammoniacal cochineal is distinguished from carminic acid by giving a beautiful purple precipitate (instead of scarlet) with "oxymuriate" of tin. The crimson, purple, and mauve colors it yields with mordants are not affected by acids so readily as those produced directly by cochineal. Ammoniacal cochineal is used in admixture with ordinary cochineal for producing the bluer shades of pinks.

Cochineal Carmine or *Carmine Lake* is a brilliant red pigment produced by precipitating a decoction of cochineal by alum or stannic chloride. Acid oxalate or tartrate of potassium may be used in conjunction with alum, but the employment of a compound of tin or aluminium appears to be essential to the production of the carmine. The employment of a decoction of cochineal itself, and not of carminic acid, is also a necessary condition, the nitro-genized matters being essential to its formation. The method by which cochineal-carmine is actually produced in practice is kept rigidly secret.[1] A sample examined by C. L i e b e r m a n (*Jour. Soc. Dyers, &c.,* i. 269) contained, after drying, 3.7 per cent. of nitrogen, only 0.25 per cent. of which could be expelled by boiling with dilute alkali. The remainder appeared to exist as proteïds, or probably in part as tyrosine.[2] The ash was white, and amounted to 8.1 per cent. 100 parts contained 43 of alumina and 45 of lime, 0.67 of oxide of tin, and small proportions of magnesia, alkalies, and phosphoric acid. The composition of the original carmine was probably approximately:—water, 17; mineral matter, 7; nitrogen-ous matters, 20; and coloring matter, 56 per cent.; with traces of wax.

Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, &c. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble.[3] The solu-tion of cochineal-carmine in ammonia yields no precipitate with ammonium oxalate, and the precipitate produced on adding an acid is a lake, from which the coloring matter can only be set free by heating with moderately strong mineral acid. If the ammo-

[1] Several recipes, collected from standard works, have been published by M. D e c h a n (*Pharm. Jour.* [3], xvi. 611). The English process is said to consist in boiling 1 lb. of cochineal and $\frac{1}{2}$ oz of potassium carbonate with 7 gallons of water for 15 minutes. The heat having been withdrawn, 1 oz. of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is de-canted, $\frac{1}{2}$ oz. of isinglass added, and heat applied till a coagulum forms, when the liquid is stirred briskly and allowed to settle.

[2] As albumin and gelatin are sometimes employed in preparing carmine, it does not follow that the whole of the nitrogen present had its origin in the cochineal.

[3] According to M. Dechan, tin spirits form with Biebrich scarlet a compound which very much resembles carmine physically and chemically, being, like it, soluble in dilute ammonia and insoluble in water. If Biebrich scarlet be present, white wool acquires a red-orange tint when boiled in the ammoniacal solution, whereas pure cochineal carmine communicates a reddish-purple shade. Biebrich carmine need not be looked for in the absence of tin.

niacal solution of carmine be heated on a water-bath, with constant stirring, until entirely destitute of ammoniacal odor, the product is a deep ruby-red liquid which gives no precipitate with mercuric chloride, and becomes purplish on addition of ammonia. Vermilionette can be recognized by treating the coloring matter with dilute sulphuric acid and agitating the liquid with ether, which on evaporation will leave the eosin in a condition ready for further examination.

The following analyses of commercial cochineal-carmine are by M. D e c h a n (*Pharm. Journ.*, [3], xvi. 511). The sample was treated with dilute ammonia, the liquid filtered, the ammoniacal solution evaporated, and the residue dried at 100°, and weighed. It was then ignited, and the ash weighed to obtain the combined aluminium, &c., the loss being regarded as coloring matter. The organic matter insoluble in ammonia appears to have consisted chiefly of starchy matters. In every case the ash was free from tin, and consisted of alumina and lime, with a trace of silica. No foreign coloring matter other than vermilion was detected.

		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Moisture, ...		22.1	16.1	2.0	22.3	20.2	23.5	8.5	10.0	21.2	13.0
Soluble in ether.	Coloring matter . .	46.1	69.2	34.1	65.7	60.8	69.5	26.1	72.0	18.4	67.5
	Alumina, lime, etc.	8.0	9.8	11.4	12.0	9.0	7.0	0.4	8.1	4.4	10.0
Insoluble in ether.	Organic matter . .	21.8	2.5	18.5	0.0	9.8	0.0	0.0	8.0	52.4	9.5
	Ash	2.0	2.4	34.0	trace	0.2	trace	14.6	1.9	3.6	trace
	Vermilion .	. .	. .	. .	. .	. .	. .	50.4	. .	. .	. .

Carmine is employed by artists, paper-stainers, and fabric-printers.

Kermes is composed of the female of the *Coccus ilicis*, an insect found on the *Ilex* or *Quercus coccifera*, a shrub growing on arid, rocky soils in hot climates. The grains are about the size of a pea, globular, and almost smooth. Kermes of good quality has a deep red color, agreeable odor, and rough, pungent taste. The red coloring matter is soluble in water and alcohol, and is either identical with or closely related to c a r m i n i c a c i d of cochineal. The decoction is turned yellowish or brownish by acids, and violet or crimson by alkalies. Ferrous sulphate blackens it, probably owing to the presence of a small quantity of tannin from the oak on which the insect lives. Kermes dyes fabrics mordanted with

alum a blood-red; with stannous chloride and cream of tartar it gives a cinnamon-yellow; and with salts of copper and cream of tartar, an olive-green. It requires about twelve times as much kermes as cochineal to produce the same scarlet with a tin mordant. Kermes is but little used in England.

Lac-Dye is the product of *Coccus lacca*, which lives on the banyan and other trees, on the twigs of which the ova are deposited. From the mature and impregnated female insects a resinous substance exudes, which encloses them. The twigs, with the attached resin and enclosed insects, are sold as *stick-lac*. If the resinous concretion be removed, powdered, and triturated with water, the greater part of the coloring matter dissolves, and the residue when dried is known as *seed-lac*. If this be melted and squeezed through cotton, it yields *shell-lac* or *shellac*. The following figures by H a t c h e t t indicate the relative composition of these three lacs:—

	Stick-lac.	*Seed-lac.*	*Shell-lac.*
Resin, ...	68.0	88.5	90.9
Coloring matter, ...	10.0	2.5	0.5
Wax, ...	6.0	4.5	4.0
Gluten, ...	5.5	2.0	2.8
Foreign bodies, ...	6.5	. .	. .
Loss, ...	4.0	2.5	1.8
	100.0	100.0	100.0

The exact method of preparing lac-dye is not generally known, but it is probably based on the treatment of stick-lac with a weak alkaline solution. The composition of the ash points to a precipitation with alum, or with lime to which some alumina has been added, probably to facilitate the washing and working up the precipitate (compare H. G. G l a s s p o o l e, *Pharm. Jour.* [3], xii. 741).

The coloring matter of lac-dye has been investigated by R. E. S c h m i d t (*Jour. Soc. Dyers, &c.*, iii. 122), who terms it l a c c a-i n i c a c i d, and points out its close resemblance to carminic acid.

Laccainic Acid, $C_{16}H_{12}O_8$, forms a brownish-red crystalline powder or crust, appearing under the microscope in well formed rhombic tables. It melts without decomposition at 180°. It is abundantly, though slowly, soluble in alcohol, and freely soluble in wood spirit, amylic alcohol, and glacial acetic acid. It is somewhat less soluble in water, with bluish-red color, and is insoluble in benzene and petroleum spirit. It resembles carminic acid in

being nearly insoluble in ether, but not precipitated on adding ether to its alcoholic solution. It is a well-defined dibasic acid, and in its reactions and the absorption-spectrum of its alkali-metal salts closely resembles carminic acid; but a difference exists between the absorption-spectra of the two substances when dissolved in strong sulphuric acid.

S c h m i d t gives the following results obtained by the analysis of two samples of lac-dye:—

	1.	2.
Moisture (expelled at 100°), ...	9.0	11.26
Mineral matter, ...	15.7	18.24
Coloring matter, ...	10.4	13.20
Other organic matter, ...	64.9	57.30
	100.0	100.00

A good lac-dye should be soft enough to be broken with the fingers, and should powder readily under the pestle. The fracture should be deep in color, not shining and resinous. When breathed on, it should emit a strong and peculiar odor. Samples which are hard and have a resinous fracture are usually poor in coloring matter, and contain an excessive proportion of resin. The amount of this constituent may be judged of from the bulk of the precipitate produced on diluting the alcoholic solution of the lac with water.

A superior variety of lac-dye is obtainable by treating stick-lac with weak ammonia, and adding stannous chloride to the solution, when the coloring matter is thrown down as a fine red precipitate. A *lac-lake* is obtained by substituting caustic soda and alum for the ammonia and tin salt in the above process. Lac-lake usually contains about 50 per cent. of coloring matter, 40 of resin, 9 of alumina, and 1 per cent. of impurities.

Lac-dye gives much the same color as cochineal, but two or three times the quantity is requisite to produce the same effect. It is prepared for dyeing by mixing it into a paste with stannous chloride and hydrochloric acid, and hence the dye and mordant are used in the same bath. Lac-reds are considered faster to light and wear and to the action of weak alkalies than cochineal reds, though they are less brilliant than the latter. The two coloring matters are sometimes employed consecutively or in admixture.

13. Analysis of Coloring Matters.

The number of dyes occurring in trade, and especially of those artificially prepared, is exceedingly great, and the difficulty of recognition consequent on their number and close resemblance is further increased by the practice of calling the same substance by several different names.

The methods of examining coloring matters with the view of identifying them require considerable modification when the dye already exists on a fibre or a fabric, as the mordant and other conditions affect its character considerably. Hence the recognition of the dyes on fabrics will be described in a separate section. In the case of a concrete coloring matter it is desirable to ascertain the shade it communicates to wool or silk, as the color which a dye will produce on a fibre can scarcely be guessed from its appearance in the solid state, and in many cases cannot even be predicted from the color of the solution.

The great point of resemblance in the generality of coal-tar dyes is that they are "substantive colors," or, in other words, will dye silk and wool without a mordant. To ascertain whether the dye is of this character it is generally only necessary to heat a fragment of white wool or a skein of white silk in a solution of the dye; usually a neutral or faintly acid solution is the best, but with alkali-blue and a few other dyes the stuff should be heated in the alkaline solution, and then removed and immersed in dilute acid, when the blue color becomes fixed. Alizarin and purpurin are not substantive colors, and hence cannot be fixed on wool or silk without a mordant.

The identification of a coal-tar dye is much facilitated by a judicious employment of certain general reagents, which will suffice to define the substance as belonging to a certain class. The color or absorption-spectrum of an aqueous or alcoholic solution of the dye is also a valuable indication, and water and alcohol may often be advantageously employed to effect a separation of mixed colors.

The following general methods of examination are of service in classifying the coal-tar colors:—

1. Agitate a small quantity of the dye with dilute sulphuric acid and ether. On separating the ether and evaporating it to dryness, a sensible residue will be left if the dye contained an acid dye, such as picric acid (or a pictrate), a nitrocresolate (Victoria yellow), a nitronaphtholate (Manchester yellow), aurin, an eosin, etc. The basic dyes are not removed from an acidulated aqueous

solution by agitation with ether, and hence a complete separation of the above-named substances may be effected by a judicious employment of this method.

2. Another indication of the nature of a dye is obtained by adding weak caustic soda to the aqueous solution and warming the liquid. Basic coal-tar dyes, except those of the safranine class (safranine, safranisol), are precipitated, while the solutions of acid dyes usually remain clear.

3. E. W e i n g ä r t n e r recommends for the distinction of soluble acid from basic dyes a reagent prepared by dissolving tannin and sodium acetate in water. The preparation and application of this reagent are described on page 481.

4. By heating with acetic acid and zinc-dust, most basic coal-tar dyes are reduced with formation of colorless l e u c o - c o m-p o u n d s, from which the coloring matters are reproducible only by the employment of moderately strong oxidizing agents. The *azo-dyes* similarly yield colorless h y d r a z o - c o m p o u n d s, but these differ from the leuco-derivatives by regenerating the original coloring matters on mere exposure to air. Somewhat different results are obtained if an alkaline reducing agent is employed, and the method, which is of special value in studying azo-dyes, is described at length on page 141.

5. J. S p i l l e r (*Chem. News*, xlii. 191) has shown that treatment of the sample with concentrated sulphuric acid affords a valuable means of recognizing coal-tar dyes, which are none of them charred by its action, except under very severe conditions. To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube with concentrated sulphuric acid. Very frequently, useful information can be gained by observing the absorption-spectrum of the colored liquid produced. The property of yielding a colorless solution with concentrated sulphuric acid, the liquid becoming colored on dilution, is a characteristic reaction of several *quinoline dyes*, and does not occur in the case of dyes of most other classes. Tabular statements of the reactions of various dyes with concentrated sulphuric acid are given under each class of dyestuffs.

6. In the case of basic dyes, the determination of the nature of the acid often materially assists identification. In most instances the basic dyes occur in commerce as hydrochlorides, but exceptions to this rule are by no means rare. To detect the salt-radical the solution of the dye should be precipitated with ammonia or

soda, and the filtered liquid acidulated with nitric acid and tested
with silver nitrate. In some few cases, especially with safranine,
the base of which is freely soluble in water, this method is not
applicable, and it is necessary to add the silver nitrate to the
acidulated solution of the original dye. Double chlorides of the
dye-base and zinc may be recognized by the presence of zinc in the
ash left on incinerating the sample. Common salt is very com-
monly present in dyes, and it is important not to mistake the
chlorine existing in this form for that existing as the hydrochloride
of a basic dye. Common salt will be left as a residue on igniting
the dye. On ignition, the eosins leave residues, the solutions of
which contain more or less haloid salts of the alkali-metals, and
hence precipitate silver nitrate. But these dyes are not basic, and
the coloring matter (containing one or more halogens in organic
combination) can be separated from the pre-existing common salt
by agitating the acidulated solution of the dye with ether (compare
page 473). The following is a list of those basic dyes liable to be
met with in commerce in other forms besides that of the hydro-
chloride:—

NAME OF DYE.	FORMULA OF BASE	FORM OF COMBINATION.
Magenta; fuchsine; rosani-line; aniline red.	$C_{20}H_{20}N_3.OH$	Acetate.
Azaleine; fuchsine.	$C_{20}H_{20}N_3 OH$	Nitrate.
Aniline blue; triphenyl-rosaniline.	$C_{20}H_{17}(C_6H_5)_3N_3.OH$	Sulphate; acetate (in alco-holic solution).
Methyl-violet.	$C_{19}H_{13}(CH_3)_6N_3.OH$	Zinco-chloride.
Benzyl-violet.	$C_{19}H_{12}(CH_3)_5(C_7H_7)N_3.OH$	Zinco-chloride.
Methyl-green.	$C_{19}H_{12}(CH_3)_6N_3.OH.CH_3Cl$	Zinco-chloride.
Iodine green; night green.	$C_{20}H_{14}(CH_3)_6N_3.OH.CH_3Cl$	Zinco-chloride.
Spirit soluble green.	$C_{20}H_{14}(CH_3)_6N_3.OH.CH_3Cl$	Picrate.
Benzaldehyde-green; mala-chite-green.	$C_{19}H_{13}(CH_3)_4N_2.OH$	Oxalate; zinco-chloride; ferrico-chloride.
Phosphine.		Nitrate.
Mauve; Perkin's purple.	$C_{19}H_{15}N_3$	Sulphate.
Nile blue.	$C_{27}H_{24}N_4$	Sulphate.
Methylene-blue.	$C_{18}H_{18}N_3O$	Zinco-chloride.
	$C_{16}H_{18}N_3S.OH$	

Nitrates, acetates, and *oxalates,* in a few cases in which they occur,
can be sought for by the usual methods, in the filtrate from the
precipitate produced on warming the dye with caustic soda. *Pic-*
rates may be sought for in the same liquid, or the original solution
may be strongly acidulated with dilute sulphuric acid, and agi-
tated with benzene or ether. The mere detection of picric acid
does not prove that the dye examined was a picrate, as free picric
acid may have been added to the hydrochloride or double zinc salt
of the base.

Many basic and other dyes are used in the form of *sulphonic acids*, and these latter bodies again are usually converted into metallic sulphonates. The sulphonates of potassium, sodium, and ammonium are the most common, but those of the metals of the alkaline earths are occasionally met with. Ammonium salts can be readily detected by the evolution of ammonia on warming the dye with caustic soda. Other sulphonates on ignition will leave metallic sulphites or sulphates, in which the metal can be readily identified. Of course, the presence of a sulphate in the ash does not prove the previous existence of a sulphonate, unless the absence of a sulphate in the original dye has been ascertained. This may usually be effected by adding barium chloride to the highly dilute aqueous solution of the dye. In the case of a colored precipitate being formed, probably consisting of the barium salt of the sulphonic acid, this should be filtered off, washed, and digested with a solution of ammonium carbonate, which will convert a sulphonate of barium into barium carbonate, without affecting barium sulphate. On again filtering, and treating the residue with dilute hydrochloric acid, any white insoluble matter will consist of barium sulphate.

The *bases* of many acid dyes can be detected without igniting by precipitating a concentrated aqueous solution of the coloring matter with pure fuming hydrochloric acid, which almost always precipitates the free acid. After filtration, the base can be sought for in the filtrate.

For the detection of the *halogens* existing in organic combination in the eosins and some other dyes, the substance should be dissolved or suspended in water, and the liquid acidulated with dilute sulphuric acid and agitated with ether. The ethereal layer is then removed, evaporated, and the residue mixed with excess of quicklime, free from chlorides, and then heated to redness in a combustion-tube. The product is treated with water, dilute nitric acid added in quantity sufficient to effect solution and leave the liquid slightly acid, the liquid filtered, and a portion of the filtrate tested with silver nitrate. If any notable precipitate is produced, chlorides, bromides, and iodides are then sought for in the usual way. In the aqueous liquid separated from the ethereal layer, metallic chlorides can be sought for directly by means of silver nitrate.

Nitro-compounds, used as coloring matters, are of a yellow or orange-red color. When warmed with metallic tin (or stannous

chloride) and hydrochloric acid, they are converted into colorless amido-compounds, which do not become again colored on exposure to air. The behavior distinguishes them, except acid naphthol-yellow, from the eosin dyes, but not from azo-colors. The latter, however, are usually sulphonates, and are not removed from their acidulated solutions by agitation with ether, as are the nitro-compounds, eosins, and most other phenolic dyes. The nitro-compounds also differ from the azo-dyes by dissolving in sulphuric acid to form yellow or colorless solutions, whereas with the latter far more brillant and striking colors are obtained. The solutions of nitro-compounds, or fibres dyed with them, are but slightly altered by hydrochloric acid (distinction from yellow azo-dyes, which are reddened); while ammonia and caustic soda tend to darken or redden the color (distinction from phosphine).

A considerable number of the coloring matters of commerce, possessing definite names, are by no means of a simple character, but are mixtures of two or more dyes. Mechanical mixtures may usually be recognized by spreading the powder on a piece of filter-paper and then floating the latter on some water or alcohol contained in a plate or flat capsule. Marks appear on the paper, and if the dye was of a simple character, these are all of the same color. On the other hand, if a mixture be under examination, the dye-particles dissolve with their respective colors, and the paper appears of two or more tints, according to the number of different coloring matters in the mixture. This appearance becomes very marked when the wet paper is held up to the light. It is even possible in this way to form an approximate notion of the relative proportions of the constituents of a mixture.[1]

When, as often happens with mixtures of azo-dyes, the constituents are too similar in shade to be recognized when dissolved side by side on filter-paper, the powdered dye should be sprinkled sparingly on the surface of pure, colorless, concentrated sulphuric acid contained in a porcelain dish. In many instances the particles will dissolve with marked differences in color. Thus a mixture of orange II (mandarin) with crocein scarlet, when sprinkled on sulphuric acid, will give carmine-red streaks alongside with others of indigo-blue color. This method of examination is very sensitive.

[1] This is sometimes of importance when it is desired to distinguish actual mixtures from dyes "ordered to shade," the latter being mostly of a simple character, but containing a slight addition of another dye, so as to give a required shade in dyeing. Thus most cheap violets contain a little magenta.

CAPILLARY ANALYSIS OF COLORING MATTERS.

Another useful method of examining certain dyes consists in dissolving the sample in the smallest possible quantity of alcohol, diluting the solution with rather more than its own measure of water, and then dropping the liquid on a piece of filter-paper, when concentric circles of different tones of color will be produced if a mixture be under examination. Magenta may be conveniently examined in this way for violaniline, mauvaniline, or chrysaniline, and the same method may be employed for testing aniline blues and violets.

The test is not at all reliable when the colors in a mixture all possess the same, or nearly the same capillarity.

A more elegant and delicate application of capillary attraction has been made by F. Goppelsroeder (*Jour. Soc. Dyers, &c.*, iv. 5), who suspends a number of strips of Swedish filter-paper in such a manner that the lower ends of the strips dip into a series of small beakers containing solutions of the dyes to be tested. The water of the solution always rises to a greater height than the coloring matter. Picric acid stands next in capillarity, and if the method be applied to a mixed solution of picric acid and turmeric, after a time three zones may be distinguished. The highest narrow zone is produced by water only; below this there is a broad yellow zone containing picric acid; while in the lowest zone only the coloring matter of turmeric exists. On exposing the paper to fumes of ammonia or dipping it in weak alkali, the presence of turmeric will be indicated by the production of a brownish-red color, while the picric acid zone will disappear. If the lowest zone be cut off, the coloring matter dissolved off with alcohol, and the process repeated with the solution obtained, the picric acid zone will be observed to be very narrow and faintly colored. Interesting results are obtained when indigo extract is examined in a similar manner. Traces of rosaniline may be detected in magenta by the same means, When an alcoholic solution of azuline was examined by the capillary test Goppelsroeder found three colored zones to be produced, namely, pink, violet, and blue. In the alcoholic solution of the blue zone, silk was dyed a much purer blue than by the original coloring matter. It is evident that the method admits of various other applications.

Patterson gives the following results on the capillary speeds of some of the more important aniline colors:

They are divided, for the sake of simplicity, into three groups,

i. e., the Rosaniline group, the Phenol group, and the Azo group. The numbers corresponding to each color represent in millimetres its capillary speed in sixty seconds. The method employed for obtaining these results was as follows.—Strips of pure, dry bibulous paper, measuring about seven and a half centimetres long by four centimetres broad, were prepared. Then a carefully-measured quantity (7.5 c.c.) of the color solution under examination, made with cold distilled water, was introduced into a beaker. The depth of this solution measured exactly five m.m. The end of one of those bibulous strips was then dropped to the bottom of the solution in the beaker, and capillarity allowed to proceed for sixty seconds exactly, when the capillary ascent of the color was then accurately noted.

I. ROSANILINE GROUP. (WATER = 14.)

Pure Magenta	2	Methyl Violet	2
Acid Magenta	14	Malachite Green	5
Acid Violet	8	Brilliant Green	4
Alkali Blue	7	Acid Green	14

II. PHENOL GROUP. (WATER = 14.)

(a) Nitro Compounds:		(β) Phthaleins:	
Picric Acid	12	Eosin	8
Naphthol Yellow S.	11.5	Uranin	11
Naphthol Green	14	Rhodamine	6

III. AZO GROUP.

(a) Oxy-azo Colors:		(β) Amido-azo Colors:	
Orange G	13	Fast or Acid Yellow	13
Tropæolin 3 O	6	Phenylene Brown	1
Tropæolin O	10		

Taking water again as the standard, the following tables of colors are obtained, arranged according to their capillary speeds:

Water	100	Acid Violet	57.1
Acid Magenta	100	Eosin	57.1
Acid Green	100	Alkali Blue	50.0
Naphthol Green	100	Rhodamine	42.8
Orange G.	92.8	Tropæolin 000	42.8
Fast Yellow	92.8	Malachite Green	35.7
Picric Acid	85.7	Brilliant Green	28.5
Naphthol Yellow S.	82.1	Methyl Violet	14.2
Uranin	78.5	Magenta	14.2
Tropæolin O.	71.4	Phenylene Brown	14.2

Although mechanical mixtures are far the most frequent, more intimate mixtures are sometimes produced by co-precipitation, or evaporation of a mixed solution. In almost all such cases one of the constituents of the mixture possesses a greater affinity for a fabric than the other, and it is this circumstance which forms the principal disadvantage of such mixtures. If a small dye-bath be

made up with the coloring matter, and small samples of wool or silk dyed successively therein until the bath is exhausted, the coloring matter, if simple, will give a shading down from one and the same color. But in the case of a mixture each consecutive sample will have a different color, and the first and last samples will be entirely different in shade. The division obtained in this way is often a very sharp one, and it becomes easy to recognize impurities in color whether due to accident or intention. The test can be conveniently conducted in a wide test-tube or small beaker, combed wool being the fibre used to withdraw the dye from the bath.

Tabular Schemes for Recognition of Coloring Matters.

Several systematic methods have been described for recognizing the various commercial coloring matters, especially those derived from coal-tar. These schemes have generally the defect of describing the coloring matters merely by their commercial names, and of being based merely on certain color-reactions. Bearing in mind the great number of dyes now met with in commerce, and the rapidity with which these disappear and are replaced by new colors, and old ones under new names, no perfect scheme of examination can be expected. A good method in many respects is that of E. Weingärtner (*Jour. Soc. Dyers, &c.*, iii. 67), who arranges artificial coloring matters in three classes :—I. Basic coloring matters soluble in water; II. Acid coloring matters soluble in water; and III. Coloring matters insoluble in water.[1]

[1] The following table shows the solubility of certain coal-tar dyes in water and alcohol, as determined by A. Brunner (*Jour. Soc. Dyers, &c.*, iii. 194):—

COLORING MATTERS.	REFERENCE PAGE.	AMOUNT DISSOLVED BY 100 PARTS OF	
		Water.	Alcohol.
Aurin,	310	almost insoluble	40
Bismarck brown,	183	3	0.35
Corallin,	311	2	0 5
Dahlia blue,		4	1
Eosin,	318	2	1
Ethyl orange,		0.02	almost insoluble
Gentian violet,		1.5	3
Luteolin,		0.28	0 6
Magenta,	276	0.3	10
Malachite green,	297	4	5
Manchester yellow,	129	2	0.15
Methylene blue,	353	3	0.15
Methyl green,	295	7	0.25
Methyl violet,	291	2	1.5
Safranine,	333	0 6	0.4
Tropæolin OO,	159	0.05	0.1
Vesuvine,	183	2	0.2

The soluble basic coloring matters are then distinguished from the acid dyes by a reagent prepared by dissolving 25 grammes of tannin and an equal weight of sodium acetate in 250 c.c. of water. This precipitates the basic dyes only. A few drops of the reagent are added to a 1 or 2 per cent. aqueous solution of the dye, and if any precipitation occur the liquid is heated, as certain sulphonated derivatives of triphenylmethane give precipitates at first which redissolve at a higher temperature.

The following are Weingärtner's tables for the recognition of artificial coloring matters. The group to which the dye belongs having been ascertained, the coloring matter may usually be identified by its special reactions. The figures in parenthesis after the names of the dyes show the pages on which more detailed information may be found respecting them:

TABLE I.—*Artificial Coloring Matters Soluble in Water. Basic Coloring Matters.*

The aqueous solution gives a precipitate with the tannin reagent.

The primitive shade reappears.					The original shade does not reappear.
Red.	Yellow or Orange.	Green.	Blue.	Violet.	
Magenta. Toluylene red. Safranines.	Phosphine. Flavaniline.	Malachite green. Brilliant green. Methyl green.	Methylene blue. New blue. Muscarine.	Methyl violet. Hofmann's violet. Mauveine. Amethyst. Crystal violet.	Chrysoïdine. Vesuvine. Auramine. Victoria blue. Methylene green (see below).
A	B	C	D	E	F

Observations.—After having reduced the basic coloring matter with zinc-powder and hydrochloric acid, the liquid should be filtered rapidly. It is very important to neutralize the filtered liquid with sodium acetate, since hydrochloric acid in excess may form with the basic color acid salts, of different color from the neutral salts.

The primitive shade does not appear on oxidation with the coloring matters in column F, but in certain cases oxidation produces different shades from the primitive. When Bismarck brown (vesuvine) and chrysoïdine are reduced, the di- and tri-amines are formed, which easily oxidize in the air with brownish-red color. It is very important to distinguish this shade from the original, which is brown or yellow. After reduction and oxidation methylene-green gives a blue shade.

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The oxidation of the reduced solution on the filter-paper may be facilitated by gently heating. Some colors oxidize with such rapidity that the original color returns whilst filtering.

M e t h y l e n e - g r e e n forms a dark green aqueous solution, which becomes quite colorless on reduction, but passes into sky-blue in presence of air. The solid substance dissolves in strong sulphuric acid with dark green color.

TABLE II.—*Artificial Coloring Matters Soluble in Water. Acid Coloring Matters.*					
The aqueous solution does not give a precipitate with the tannin reagent.					
The solution is decolorized.					The solution becomes brownish-red. The color of the ammoniacal solution reappears on the paper.
The original color reappears on paper.		The original color does not appear.			
The aqueous solution is acidulated with hydrochloric acid, and treated with ether.		The coloring matter, when heated on platinum foil,			Alizarin S. Alizarin blue S. Cœrulein S.
The ether dissolves the coloring matter, and the solution immediately becomes colorless.	The ether remains colorless.	Deflagrates without formation of colored vapors.	Burns quietly, or slightly deflagrates, giving off colored vapors. Heat a piece of calico, not mordanted, in the aqueous solution.		
Phthaleïns. Eosins. Aurin.	Sulphonated rosanilines. Sulphonated indulines.	Nitro-coloring matters.	The coloration of the dye is fast to warm soaping.	The color does not resist warm soaping.	
			Azo-colors from benzidine, &c.	Azo-colors. Tartrazin. Erythrosin.	
G	H	I	J	K	L

Observations.—*a.* The reduction of the acid yellow, orange, ponceau, and claret non-fluorescent colors requires special precautions. The best way is to treat with zinc-powder and hydrochloric acid, and afterwards to neutralize with sodium acetate, as has already been pointed out. The reduction will often be too slow if ammonia or acetic acid be used.

b. It is necessary, as before, to compare with great care the original color with that which is produced by reoxidation, so that their identity or difference may not be mistaken. In the reduction of nitro- or azo- bodies diamines or amidophenols are formed, which by oxidation give dirty or brown shades. In the column K this remark equally applies to erythrosin, for when that coloring matter is reduced iodine is separated and fluorescin formed.

c. All the coloring matter not specified in *a* are reduced by zinc and ammonia.

d. When the acid colors are being reduced, the solution, as long as zinc-powder is present, should be colorless, or at most slightly yellow or red.

e. The nitro-derivatives of the azo-coloring matters and of fluoresceïn can be easily recognized by the formation of "Pharaoh's serpents" on heating a small quantity (0.5 grm.) on platinum foil.

f. In order to find the group NO_2 with certainty in a yellow coloring matter (*e. g.*, picric acid), it is necessary to add a little sodium carbonate.

g. It is very difficult completely to reduce alizarin S. It is therefore put in column L. The color of the ammoniacal solution more often returns, but if the reduction has been carried too far that color does not reappear.

TABLE III.—*Artificial Coloring Matters Insoluble in Water.*						
The coloring matter is treated with water, and a little 5 per cent. solution of caustic soda added.						
The coloring matter dissolves.		The coloring matter does not dissolve. It is heated with 70 per cent. alcohol.				
The alkaline solution is filtered, treated hot with zinc-powder, and then poured on a filter-paper.						
The color of the alkaline solution reappears.	The color of the alkaline solution does not reappear, or the solution changes color during the reduction, which color lasts.	It is dissolved.				It is not dissolved.
		The alcoholic solution is not fluorescent. Add a little 33 per cent. soda solution.		The alcoholic solution is fluorescent. Add a little 33 per cent. soda solution.		Indigo.
Cœruleïn (in paste). Galleïn. Gallo-cyanin. Galloflavin.	Canarin. Alizarin. Anthrapur-purin. Flavopur-purin. Nitroalizarin. Alizarin blue. Chrysamine. Solid green.	The color changes to red-brown.	The color does not change.	The fluor-escence disap-pears.	The fluor-escence persists.	
		Indulines. Nigrosines. Rosaniline blue. Diphenyla-mine blue.	Indo-phenol.	Magdala red.	Primrose, Cyanosin.	
M	N	O	P	Q	R	S

In some respects the method of O. N. Witt (*Jour. Soc. Dyers*, etc., ii. 64; *Analyst*, xi. 111) is preferable to that of Weingärtner. It is given in the following tables:

RED COLORS.

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL AND ETHER.	ZINC POWDER.	GENERAL REMARKS.
Carminaphtha.			Reddish-violet.	Solution in alcohol, salmon red, without any fluorescence.		This dye is not much known; it is manufactured by L. Durand and Huguenin, and is used to a small extent in calico printing.
Magdala Red. (Naphthaline Rose.)			Greenish-gray, turning red on dilution with water. A reddish-violet precipitate forms afterwards.	Solution in alcohol, bluish-red with intense orange-red fluorescence.		Spectroscope shows a broad absorption band, which completely extinguishes the yellow and green of the spectrum.
Quinoline Red.	Insoluble in cold, rather easily soluble in hot water.		Colorless; on dilution, every drop of water produces an intense red, which disappears on stirring. On diluting sufficiently, the whole is colored deep magenta.	As with Magdala-red.		Spectroscope shows absorption band rather more to the right, so that some of the yellow remains. The reaction with H_2SO_4 differs entirely from that in case of Magdala-red. The property of yielding colorless solution with concentrated H_2SO_4, which becomes colored in dilution, is a characteristic reaction of several quinoline dyes, and does not occur with dyes of other classes.
Eosins. Soluble in Alcohol.			Lemon-yellow to orange. No striking change of color on dilution.	Solution in alcohol is fluorescent likewise, but the fluorescence is greener.		The different Eosins may be distinguished by the shades they give when small samples are dyed.
Rhodinins. (Indulines of the Naphthaline series.)			Green, turning bluish-red on dilution.	Solution in alcohol, dull bluish-red.		

I.—Insoluble in cold water, likewise in hot water, or but slightly so. Easily soluble in alcohol.

RED COLORS.—*Continued.*

Name.	Solution in Water.	Reactions.	Solution in Concentrated H₂SO₄.	Solution in Alcohol and Ether.	Zinc Powder.	General Remarks.
Fuchsine. (Rubin, Magenta, Aniline Red.)	Bluish red.	Solution in water is turned yellowish-brown by HCl or H₂SO₄, but the red color is restored by sodium acetate.	Dissolves with a yellowish-brown color.		Solution in water permanently decolorized.	In a dilute solution, to which ammonia has been added, and which is only pale red, wool is dyed a deep red on boiling. The sample either consists of distinct green crystals, or of a metallic-green powder.
Toluylene Red. (Neutral Red.)	Bluish red.	Ammonia precipitates orange-colored flakes, which are dissolved by ether red, with a yellow fluorescence.	Green, changing on dilution through blue and violet to red.			The product is generally very impure, and will give these reactions with dirty colors.
Gallein.		On addition of caustic soda to the solution in water, the color changes to intense blue.	Brownish yellow somewhat redder on dilution.			
Saffranine and Saffranisol.		Addition of alcohol to the solution in water causes a distinct grayish-yellow fluorescence, not precipitated by addition of acids.	Green changing on dilution through blue to red.		Decolorized, but the original color is immediately restored on admission of air.	Distinguish these two products by the shade given in dyeing.
Eosin.	Pure red, with a greenish yellow fluorescence, which becomes all the more distinct as more water is added.	Acids precipitate orange-yellow flakes, which are soluble in ether.	Pure yellow.	Solution in ether pure yellow without fluorescence.		

Basic Dyes. (a) Precipitated by caustic soda.

Acid dyes or basic dyes of the saffranine class. (b) Not precipitated by caustic soda.

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

RED COLORS.—*Continued.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL AND ETHER.	ZINC POWDER.	GENERAL REMARKS.
Eosin Scarlet. (Bromnitro Fluorescein.)	Of a more bluish-red than with Eosin, and is without any fluorescence.	Acids give a straw-yellow precipitate.	Golden yellow.	Solution in ether straw yellow.	Zinc powder decolorizes a solution a solution which has been treated with ammonia. On sprinkling the decolorized solution upon blotting paper it is turned an intense blue by the action of the air. (Distinction from Eosin.)	
Phloxin. *Rose Bengale.*	Bluish-red without fluorescence.	Acids give an orange-yellow precipitate, which is soluble in ether.	Orange yellow.		Zinc powder and ammonia decolorize but the color does not return, or but very slightly on admission of air.	Distinguish these two products by the shade.
Biebrich Scarlet. (Double Scarlet.)	The concentrated solution in hot water stiffens on cooling to a jelly.	Acids give a brown flaky precipitate.	Grass green; gives on dilution, first a blue color, and then a dirty brown precipitate.		On warming with zinc powder and ammonia, the solution is turned first pure yellow and then colorless.	

Acid dyes or basic dyes of the safranine class.

(b) Not precipitated by caustic soda.

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

RED COLORS.—*Continued.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL AND ETHER.	ZINC POWDER.	GENERAL REMARKS.
Crocein Scarlet 3 B.	Indigo blue changing on dilution through violet into red.	Barium chloride added to a solution in water gives a flaky-red precipitate, which on boiling becomes suddenly crystalline and deep violet-black.				
Congo Red.	If cotton is boiled in the water solution, with or without a small addition of soap, it is dyed a red color, which will stand washing.	The slightest trace of acid added to a solution in water changes it to a pure blue.	Slate blue, no change on dilution.			
Xylidine Ponceau.	The solution in hot water stiffens on cooling, with separation of bronze-colored shining crystals.		Violet; brown precipitate on dilution.			This product is prepared from alpha naphtholsulphonic acid, according to German patent 26012.
Crocein Scarlet. 7 B. Extra.		Concentrated solution in water, treated with magnesium sulphate, yields on cooling, long silky needles of the magnesium salt.	Violet.			Dyes wool a beautiful scarlet-red. This dye is produced by the action of diazo-naphthionic acid upon the crocein - beta - naphtholsul-phonic acid.

Acid dyes or basic dyes of the safranine class.
(b) Not precipitated by caustic soda.

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

RED COLORS.—*Concluded.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL AND ETHER.	ZINC POWDER.	GENERAL REMARKS.
Ponceau R., 2 R., 3 R., Anisol Red. Coccin.		Calcium chloride and barium chloride give an amorphous flaky precipitate from the solution in water.	Pure rose colored or carmine red; on dilution a brownish-red precipitation.			These colors, from beta-naphtholdisulphonic acids, may be distinguished by the shade given in dyeing. Coccin; German patent 3229.
Acid Azo Rubin.		An addition of calcium chloride to a solution in water, gives a red flaky crystalline precipitation.	Bluish - violet; red on dilution.			Dyes wool a magenta red. German patent 26012.
Fast Red. (Rocceilline.)	Deep brownish-red.	The addition of a drop of saturated soda solution to a concentrated boiling solution of the dye in water, precipitates the soda salt of the dye in the form of sparkling brown scales.	Blue; on dilution a yellowish-brown precipitate.			Dyes wool a deep brownish-red.
Bordeaux B.	Claret red.	Calcium chloride and barium chloride give flocculent amorphous precipitates.	Indigo blue.			German patent 3229.
Acid Magenta.	Beautiful blue red.	The solution in water is completely decolorized by caustic soda, but the original color is restored by acetic acid.				

(b) Not precipitated by caustic soda.
Acid dyes or basic dyes of the safranine class.

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

GREEN COLORS.

NAME.	SOLUTION IN WATER.	REACTIONS, ETC.	SOLUTION IN CONCENTRATED H_2SO_4.	GENERAL REMARKS.
Cœrulëin.	But slightly soluble in water, with o l i v e - brown color.	On addition of an alkali, plentiful solution w i t h grass-green color.	Dirty-brown color.	
Victoria Green. *Brilliant Green.*	Easily soluble, with beautiful green color.	Alkalies effect a rose-colored or gray precipitate; strong acids color solution yellow.	Yellow.	Distinguished by the shade obtained in dyeing.
Iodine Green. *Methyl Green.*	Easily soluble, with beautiful blue-green color.	Acids impart a yellow color; alkalies decolorize without a trace of precipitation.	Yellow.	A dyed sample, on being heated above 100° C., is turned violet. Methyl green dyes in a neutral bath.
Greens from the Sulphonic Acids of Oil of Bitter Almonds. Malachite Green. L i g h t Green, S. Acid Green, Helvetia Green.	Easily soluble, with a proportionately weak green color.	Acids first intensify the color and on further addition turn to a yellow; alkalies decolorize completely.	Yellow.	Silk and wool (the latter after treatment with sulphuric acid) can only be dyed in an acid bath (distinction from m e t h y l g r e e n). Dyed samples will sustain a heat of 150° C. for a short time without damage.

VIOLET COLORS.

NAME.	SOLUTION IN WATER.	REACTIONS, ETC	SOLUTION IN CONCENTRATED H_2SO_4.	GENERAL REMARKS.
Regina Purple. Diphenylrosaniline.	Sparingly soluble.		Cinnamon brown.	Soluble in alcohol.
Methyl Violet, R–6 B. Hofmann's Violet.	Easily soluble.	Alkalies give a precipitate, hydrochloric acid imparts first a green and then a yellow color.		Distinguished by the shades.
Mauvein. (Perkin's Violet, **Rosolane.**)	Not very easily soluble.	Alkalies effect a violet precipitation.	Gray color, on dilution successively grayish-green, sky-blue, bluish-violet, red-violet.	
Lauth's Violet. (Thionine.)	Soluble.	Acids give a pure blue precipitate, alkalies a red-violet one.	Emerald-green, on dilution sky-blue.	Zinc powder in acid as well as ammoniacal solution forms a splendid vat.
Galloeyanin.	Soluble on boiling.	Hydrochloric acid imparts a pure carmine-red color.	Blue color, redder on dilution.	
Amethyst. Fuchsia. Girofle.	Solution; red violet.	Addition of alcohol produces a carmine-red fluorescence.	Emerald-green color, on dilution blue or violet.	Violet saffranine colors; ethylated and methylated homologues of phenol saffranine.

The foregoing collection includes most dyes which are now, or have been, up to a recent date in the trade. It should be an easy matter to introduce any which have been overlooked, or which may be brought out shortly, according to their distinguishing characteristics.

BLUE COLORS.

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	ZINC POWDER.	GENERAL REMARKS.
Rosaniline Blue. Diphenylamine Blue.	Quite insoluble.	Hydrochloric acid leaves the solution in alcohol unchanged, but for the precipitation of microscopic shining green crystals; caustic soda changes colors to brownish-red.	Light-red brown.	Dissolves with a blue color of varying shade.		Distinguished by dyeing on silk, and especially on comparing by artificial light.
Indophenol.	Insoluble.	The solution in alcohol is colored red by hydrochloric acid, but is unchanged by alkalies.		Soluble.		
Methylene Blue.	Easily soluble.	Hydrochloric acid gives a greenish precipitate; caustic soda a violet-red precipitate.			Reduced by zinc powder; the color being restored on access of air.	Contains zinc.
Victoria Blue.	Rather easily soluble.	Acids impart a yellowish-brown color; alkalies form a red-brown precipitate.				
Alkali Blues. R—6 B. (Nicholson's Blues.)	Easily soluble.	Alkalies decolorize almost completely.				Distinguish by the shade. Wool attracts the dye from the alkaline solution, and after washing with water is dyed a deep blue by dilute acids.
Water Blues. R—6 B.	Easily soluble.	Alkalies do not form a precipitate in the aqueous solution.			Decolorize permanently.	Wool is dyed in an acid solution.
Indigo Carmine. (Indigo extract.)	Easily soluble.	Dilute nitric acid decolorizes permanently on boiling.			Zinc powder and ammonia form a vat—i. e., the color is restored on access of air.	Only dyed in an acid bath.
Indulines. R—6 B.	Insoluble.	Solution in alcohol is colored brownish-red to violet by alkalies.	Blue color.	Soluble.		The more soluble, the redder the shade.

BLUE COLORS.—*Concluded.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	ZINC POWDER.	GENERAL REMARKS.
Indulines, Soluble in Water.	Soluble.	Acids form a blue precipitate; alkalies a red to violet coloration; dilute nitric acid does not decolorize even on warming.			Zinc powder and ammonia form a vat.	Distinguish by the shade.
Leucindophenol.		Caustic soda imparts a blue color immediately on access of air.				The commercial product gives a gray paste.
Orthonitro-phenylene. Propiolic Acid.		Soluble on addition of caustic soda without formation of blue color.				The commercial product forms a gray paste. An addition of grape sugar and boiling gives rise to the separation of indigo blue in crystals.

YELLOW AND ORANGE-RED COLORS.

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	GENERAL REMARKS.
Chinaphtalon.		Solution is not affected by acids or alkalies; at most the color is rather deepened.		Lemon yellow.	
Turmeric dye.		Solution is left unchanged by acids; alkalies and boracic acid turn the same a deep brown-red.		Golden yellow.	
Dimethylamido-azobenzol.		Hydrochloric acid produces a red coloration. In a solution which has been treated with HCl, amyl nitrite produces neither change of color nor evolution of nitrogen on boiling.		Golden yellow.	This color has been employed to dye artificial wax, prepared from ozokerit.
Amidoazobenzol.		Reaction same as in last-named, except that amyl nitrite produces a change of color and a weak evolution of nitrogen.		Golden yellow.	

1.—The dye is insoluble in cold water, likewise not in water, or but difficultly soluble. Soluble in alcohol.

YELLOW AND ORANGE-RED COLORS.—*Continued.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	GENERAL REMARKS.
Picric Acid.	Greenish-yellow; tastes very bitter.	Alkalies turn solution a dark yellow; acids effect no change.			
Martius' Yellow.	Golden yellow.	Acids form a whitish precipitate.			See note in introduction.
Acid Naphthol Yellow.	Golden yellow.	Not precipitated by acids. Potassium chloride causes a crystallization of needles.			
Fluorescein. (Uranin.) *Benzifluorescein.* (Chrysoline.)	Brownish-yellow; a splendid green fluorescence	Acids cause the fluorescence to disappear, and they also form a precipitate.			These two dyes can only be distinguished by an exact investigation of the separated dye-acids.
Chinolin Yellow. (Chinaphtalene sulpho acid.)	Golden yellow.	Not precipitated by acids.			Not decolorized by zinc powder and ammonia, nor by stannous chloride and hydrochloric acid.
Phosphine.		Yellow; flaky precipitate with alkalies; which is soluble in ether with a pure yellow color and a splendid green fluorescence.			The extremely delicate ether test permits of phosphine being easily and surely recognized in mixtures with grenadine, maroon, etc.
Flavaniline.		Milky-white precipitation by alkalies, which is dissolved again by ether—colorless with a greenish-blue fluorescence.			
Auramine.		Milky-white precipitation by alkalies, which is dissolved again by ether—colorless and without any fluorescence.			The yellow solution of the dye becomes less and less intense on boiling with hydrochloric acid, and finally is colorless.

Acid Dyes.
(b) Caustic soda gives a precipitate. (a) No precipitate with caustic soda.

Basic Dyes.
II.—The dye is plentifully soluble in water, especially boiling. Dissolved in concentrated sulphuric acid without any intense coloration.

YELLOW AND ORANGE-RED COLORS.—*Continued.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	GENERAL REMARKS.
Chrysoïdin.	Solution of the dye in water forms a blood-red jelly on cooling.		Brownish-yellow.		Dyes wool yellow.
Vesuvin. (Bismarck Brown. Phenylene Brown.)	The solution does not gelatinize on cooling.		Brown.		Dyes wool orange-brown.
Fast Yellow.	Yellow.		Yellow; salmon-red on dilution.		
Methyl Orange. Ethyl Orange.	Yellow; crystallizes on cooling in glittering gold colored scales.	Dilute acids give a glittering red-violet precipitate.	Yellow; carmine-red on dilution.		
Tropæolin OO. (Diphenyl-amine Yellow.)	Yellow; crystallizes on cooling.	Calcium chloride and barium chloride give perfectly insoluble precipitates.	Violet; red violet on dilution, with a simultaneous formation of a steel-gray precipitate.		
Yellow N. (Poirrier.)	Yellow; crystallizes on cooling.	Barium chloride precipitates a yellow salt, which crystallizes out of excess of water in shining leaflets.	Bluish-green; violet on dilution, with steel-blue precipitation.		

(*a*) Caustic soda gives a precipitate.

(*b*) Caustic soda gives no precipitate.

III.—The dye is soluble in water; the solution in sulphuric acid is of an intense color.—*Azo Dyes.*

YELLOW AND ORANGE-RED COLORS.—*Concluded.*

NAME.	SOLUTION IN WATER.	REACTIONS.	SOLUTION IN CONCENTRATED H_2SO_4.	SOLUTION IN ALCOHOL.	GENERAL REMARKS.
Luteolin.	Yellow; crystallizes on cooling.	Calcium chloride gives an orange precipitate, which becomes red and crystalline on boiling.	Yellowish-green; violet on dilution, with a gray precipitate.		
Citronin. (Jaune Indien, Curcumin.)	Yellow; generally dull.	The solution in water is turned deep red to violet on being treated with alcoholic caustic soda.	Carmine-red; yellow on dilution.		
Orange G.	Orange.	Calcium chloride produces a splendid crystallization of the calcium salt in leaflets.	Deep orange; no change of color on dilution.		German patent 3229.
Tropæolin O.	Yellow.	Addition of a little hydrochloric acid effects crystallization in yellow leaflets; addition of more acid, the separation of the free acid in gray needles.	Brownish-orange; no change of color on dilution.		
Orange II. (Beta-naphthol Orange, Mandarin.)	Red orange.	Calcium chloride precipitates the beautiful red calcium salt, which crystallizes in needles out of an excess of boiling water.	Carmine-red; orange on dilution.		
Tropæolin OOO. Orange I.	Red orange.	Caustic soda turns the solution in water to a carmine-red.	Violet; orange on dilution.		

(b) Caustic soda gives no precipitate.

III.—The dye is soluble in water; the solution in sulphuric acid is of an intense color.—*Azo dyes.*

The analytical tables of Weingärtner and Witt, however, have some serious faults. In many cases the reduced colors (the rosanilines for example) are only reoxidized by the air with extreme slowness, and therefore may at times be mistaken for other colors. Also, since the publication of these tables, a large number of new dyestuffs have appeared, and considerable modifications are necessary. A. G Green (*Jour. Soc. Chem. Ind.*, xii. No. 1), taking Weingärtner's system as a basis, has constructed a scheme of analysis which is given in the following tables. For group reagents he employs:

1. A solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate.

2. Zinc dust and dilute hydrochloric acid, or zinc dust and aqueous ammonia.

3. Solution containing 1 per cent. of chromic acid (for basic colors).

4. Solution containing 1 per cent. of chromic acid or potassium bichromate and 5 per cent. of sulphuric acid (for acid colors).

The members of the same group are distinguished from each other by their behavior towards aqueous acids and alkalies, concentrated sulphuric acid, alcohol, etc., and by their dyeing properties. See the reactions of the various colors as given by Witt, Weingärtner, and others.

GROUP I.—DYESTUFFS SOLUBLE IN WATER.

A.—Precipitated by Tannin Solution: Basic Colors.

The aqueous solution is reduced with zinc dust and hydrochloric acid and a drop of the decolorized solution put on filter paper. If the color does not quickly return on exposure to air, the spot is touched with a drop of 1 per cent. chromic acid solution.

The original color quickly reappears on exposure to air: *Azine-, Oxazine-, Thiazine-,* and *Acridine Colors.*					The color appears very slowly or not at all on exposure to air, but returns on spotting with 1 per cent. chromic acid solution: *Triphenylmethane Colors,* and *Basic Phthaleïns.*				The original color does not return at all.
Red.	Orange and Yellow.	Green.	Blue.	Violet.	Red.	Green.	Blue.	Violet.	Yellow and Brown.
Toluylene Red. Safranine. Pyronine. Acridine Red.	Phosphine. Benzofla- vine. Acridine Yellow. Acridine Orange.	Azine Green.	Methylene Blue. New Methyl- ene Blue N. Thionine Blue. Toluidine Blue. Meldola's Blue. Muscarine. Neutral Blue. Basle Blue R & B B. New Methyl- ene. Blue G G. Nile Blue. Capri Blue. Fast Black. Indazine M. Metaphenyl- ene Blue B. Paraphenyl- ene Blue. Indamines.	Mauve. Amethyst. Neutral Violet. Fast Neutral Violet. Prune. Paraphenyl- ene Violet. Indamines.	Magenta. Isorubine. Rhoda- mine.§	Malachite Green. Brilliant Green. Methyl Green. Iodine Green.	Victoria Blue B.* Victoria Blue 4 R. Night Blue.	Methyl Violet. Crystal Violet. Hofmann Violet. Benzyl Violet. Ethyl Purple. Regina Purple.	Auramine.† Thioflavine T.‡ Chrysoïdine. Bismarck Brown.

* The shade which returns is much greener than the original.
† The reduced solution gives a beautiful violet when the spot on filter paper is warmed over a flame till dry.
‡ Is only reduced with difficulty and very slowly.
§ The color returns more quickly than with the rosanilines.

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B.—Not Precipitated by Tannin Solution: Acid Colors.

The aqueous solution is reduced with zinc dust and hydrochloric acid, or with zinc dust and ammonia, and a drop of the decolorized solution is put on filter paper. If the color does not quickly return on exposure to air, the spot is touched with a drop of chromic acid solution (1 per cent. CrO_3 + 5 per cent. H_2SO_4), warmed over a flame, and then held in the vapor of ammonia.

The solution is decolorized.			The original color does not return at all: Azo-, Nitro-, Nitroso-, and Hydrazine Colors.		Not decolorized (by zinc and ammonia, but changed to brownish-red. Original color returns quickly on exposure to air.	Very slowly and incompletely decolorized (zinc and ammonia).	Not altered by zinc and ammonia; very slowly or not at all by zinc and hydrochloric acid.
The original color quickly reappears on exposure to air.	The original color does not reappear on exposure to air, or only very slowly, but returns with chromic acid, and exposure to ammonia vapor.		Heated on platinum foil.				
	The aqueous solution of the dyestuff is acidified and shaken with ether.						
	The ether extracts the color-acid, leaving the solution nearly colorless:—	The ether remains colorless:	Deflagrates with production of colored vapors: Nitro-colors:—	Burns quietly or deflagrates slightly, giving off colored vapors:—Azo-, nitroso-, and hydrazine colors.			
				The color dyed upon unmordanted cotton.			
				Resists warm soap. — Is stripped by warm soap.			
Sulphonated azines, oxazines, thiazines, &c.:— Soluble Indulines.* Soluble Nigrosines.* Resorcin Blue. Azurine. Thiocarmine. Basle Blue R S and B B S. Gallamine Blue. Gallocyanine. Gallanilic Indigo P S. Indigo-carmine. Saffrosine. Azo-carmine. Mikado Orange.*	*Phthaleïnes and Aurine:—* Uranine. Chrysoline. Eosine. Erythrine. Phloxine. Erythrosine.† Rose Bengale.† Cyclamine. Aurine. Coralline. / *Sulphonated triphenylmethane colors:—* Acid Magenta. Acid Violets. Formyl Violet. Alkali Blues. Soluble Blues. Patent Blue. Fast Green, bluish. Acid Greens. Guinea Green. Chrome Violet.		Picric acid. Victoria Yellow. Aurantia. Martius Yellow. Naphthol Yellow S. Brilliant Yellow. Aurotine.	Substantive Azo-colors. — Ordinary Azo-colors. Naphthol Green B. Tartrazine.	Alizarin S. Alizarin Blue S. Cœruline S.	Clayton Yellow. Thiazol Yellow. Turmerine. Mimosa.	Quinoline Yellow S. Primuline. Thioflavine S. Oxyphenine.

* If the reduction is carried too far, the color does not return.   † Iodine is separated by the chromic acid, but disappears on exposure to ammonia.

GROUP II.—DYESTUFFS INSOLUBLE IN WATER.

The powder or paste is treated with water and a few drops of 5 per cent. caustic soda solution.

The color dissolves.		The color remains insoluble.				
The alkaline solution is heated with zinc dust and ammonia, and a drop is put on filter-paper.		Soluble in 70 per cent. alcohol.				Insoluble in 70 per cent. alcohol.
		Solution not fluorescent.		Solution fluorescent.		
		On adding caustic soda (33 per cent.) to the alcoholic solution.		On adding caustic soda (33 per cent.) to the alcoholic solution.		
Decolorized or changed to light-brown. The original color returns very quickly on exposure to air.	Decolorized or changed to brown. The original color does not reappear on exposure to air.	Color becomes reddish-brown.	Color not altered.	Fluorescence destroyed.	Fluorescence remains.	
Cœruleine.	Alizarine.	Induline.	Indophenol.	Magdala Red.	Spirit Eosins.	Indigo.
Galleïne.	Anthropurpurine.	Nigrosine.	Sudan II and III.		Cyanosine.	Aniline Black.
Gallocyanine.	Flavopurpurine.	Rosaniline Blue.	Carminaphth.			Primuline Base.
Gallanilic Violet B S.	Alizarine Orange.	Diphenylamine Blue.				
Gallanilic Blue P.	Alizarine Brown.					
Galloflavine.	Alizarine Bordeaux.					
Alizarine Blue.	Alizarine Yellow G G and R. Chrysamine.					
Alizarine Black.	Sudan Brown.					
Alizarine Cyanine.	Patent Fustin.					
Rufigallol.	Myrtle.					
	Gambine R and Y Dioxine.					

The reduction with zinc-dust is best made by adding a little of the zinc-dust to the hot solution of the dyestuff contained in a test-tube, agitating, and then adding dilute hydrochloric acid drop by drop until decolorized.   Any excess of acid should be carefully avoided.   In some cases when the color acid is very insoluble, the reduction should be made with zinc-dust and ammonia.   When the reduced solution is poured from the excess of zinc-dust on a piece of white filter-paper, and exposed to the air, filtration is unnecessary, as the presence of a little zinc upon the paper does not interfere with the oxidation.   If the color does not return in a minute or two, the paper should be touched with a drop of the chromic acid solution (with addition of sulphuric acid for acid colors).

In case of the latter dyestuffs, the paper, after being spotted with chromic acid, should be held over a bottle of strong ammonia, because some acid colors, like the eosins, do not show their true color while acid.

A. G. R o t a (*Chem. Zeit.*, xxii. 437) gives a systematic scheme for the analysis of dyestuffs, based on the chemical constitution of the dyestuff.   In accordance with the views of Nietzki and Armstrong, the organic dyestuffs are regarded as quinone derivatives; those having the structure of mono- and di-amidoquinones are capable of reduction by stannous chloride, while those in which the oxygen atom of the quinone is replaced by a divalent hydrocarbon group are not reduced.   Thus, regarding $O = R = O$ as representing an ortho- or paraquinone, the nitroso-, azo-, and imidoquinone dyestuffs represented by $O = R = N —$ or $— N = R = R —$ are reducible, but the oxyquinone and triphenylmethane dyestuffs having the composition $O = R = C =$ and $— N = R = C =$ are not reducible.

The reduced coloring matters can be subdivided into two groups, according to whether the color is restored on oxidation with ferric chloride; and the unreduced coloring matters can also be subdivided according to their behavior on treatment with caustic potash.

The reduction is carried out in an aqueous or alcoholic solution of the dyestuff diluted to about $1 : 10,000$.   Of this solution 5 c.c. are treated with 4–5 drops of concentrated hydrochloric acid and the same amount of a 10 per cent. solution of stannous chloride. The mixture is shaken, and, if necessary, heated to the boiling-point.   If not entirely decolorized, the solution should be diluted still further and more stannous chloride added.

A. Classification of Organic Coloring Matters.

A portion of the aqueous or diluted alcoholic solution treated with HCl and SnCl₂.

Complete decolorization.[1] Reducible coloring matters. The colorless solution after neutralization with KOH is treated with Fe_2Cl_6, or shaken with exposure to the air.		The color is changed no further than with HCl alone. Non-reducible coloring matters. A part of the original solution is mixed with 20 per cent. KOH and warmed.	
The liquid remains unchanged. Coloring matters not reoxidizable.	The original color restored. Reoxidizable coloring matters.	Decolorization or a precipitate. Imido-c a r b o - q u i-none coloring matters.	No precipitation. The liquid becomes more colored. Oxy-carbo-quinone coloring matters.
CLASS I.	CLASS II.	CLASS III.	CLASS IV.
Nitro-, nitroso-, and azo coloring matters, including azoxy-and hydrazo-colors.	Indogenide- and imido-quinone coloring matters.	Amido-derivatives of di- and tri- phenylme-thane, a u r a m i n e s, acridines, quinolines, and color derivatives of thiobenzenyl.	Non-amido diphenyl-methane c o l o r i n g matters, oxy-ketone coloring matters (most of the natural organic coloring matters).

[1] Some indulines are only decolorized with difficulty, the solution never becoming quite colorless.

Table B.

Group I.—Dyestuffs Reducible with Stannous Chloride and Hydrochloric Acid, the Color not Returning on Oxidation.

Nitro-dyestuffs R.NO₂. Yellow or orange dyestuffs soluble in water, dyeing wool and silk directly, but not cotton. The aqueous solution tends to decolorize with hydrochloric acid. On partial reduction with hydrochloric acid and stannous chloride, they give red nitro-amido derivatives (nitramines) or nitrophenols turning red in KOH . . . .

- Nitramines soluble in ether in presence of KOH . . . $\;.N:R:N\!\!<^{O}_{OH}$ — *e. g.* Aurantia.
- *Nitrophenols* insoluble in ether in presence of KOH . . .
  - *Unsulphonated*, soluble in ether, in presence of acetic acid . . . . . . $\left.\right\}\;O.R:N\!\!<^{O}_{H}$ — *e. g.* Victoria Yellow. Naphthol Yellow S.
  - *Sulphonated*, in every case insoluble in ether.

Nitroso-dyestuffs O:R:N.OH. Brown or green, usually insoluble in water. Dye indirectly. Give a blue colcration with sulphuric acid and phenol (Liebermann's reaction) . . . .

- *Unsulphonated*, insoluble in alcohol, soluble in ether in presence of acetic acid . . . . . . — *e. g.* Dioxine.
- *Sulphonated*, soluble in water, insoluble in ether . . . . . . — *e. g.* Naphthol Green B.

Azo dyestuffs R.N:N.R. Recognizable as not belonging to either of the two foregoing subdivisions. Their aqueous solution treated with KOH and extracted with ether behaves as follows . . . .

- The solution is colored, the color being extracted by dilute acetic acid, *Basic dyestuffs*.
  - Unsulphonated amido-azo dyestuffs . . . . . . $\left.\right\}\;.R.N:N.NHR'$ — *e. g.* Bismarck Brown.
- Colored solution. The color is not extracted by dilute acetic acid. *Neutral dyestuffs**.
  - Oxyazo dyestuffs not containing a carboxyl group. . . . . $\left.\right\}\;O.R.N:N.R'$ — *e. g.* Sudan I.
- Colorless solution, acetic acid does not extract anything. *Acid dyestuffs* . . .
  - *Unsulphonated*, soluble in ether from dilute acetic acid . . .
    - Oxyazo dyestuffs with a carboxyl group. . . . → Dye cotton indirectly. — Diamond Yellow.
    - Non-amidated, unchanged by HNO₂† . . . → Dye cotton directly. — Chrysamine. Bordeaux B. Azo Blue.
  - *Sulphonated*, insoluble in ether from dilute acetic acid . . .
    - Amidated, react with HNO₂ . . . → Dye cotton indirectly. — Fast Yellow N.
    - . . . → Dye cotton directly. — Congo Red.

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* Some amido-azo dyestuffs (Aniline Yellow) behave like neutral dyestuffs, but differ from these in being decolorized by nitrous acid.

† The presence of an amido group is detected by treating 5 c.c. of the warm solution with 2-3 drops of a 1 per cent. dilute acetic acid and the same quantity of a 1 per cent. potassium nitrite solution. Amido derivatives are decolorized or the color is modified whilst non-amidated compounds remain unchanged or are not further affected than by acetic acid alone.

TABLE C.

Group II.—Dyestuffs Reducible with Stannous Chloride and Hydrochloric Acid, the Color Returning on Oxidation.

The aqueous or alcoholic solution (5 c.c. of a strength 1:10,000), is treated with 4-5 drops of a 20 per cent. KOH and extracted with 10-15 c.c. of ether. This solution washed with water (once with an equal volume if the original solution was aqueous, but 2-3 times if alcoholic), shows the following reactions:

The solution is colored or colorless, but imparts the original color to 5 per cent. acetic acid when shaken with it. Basic Dyestuffs.—Dye wool from an alkaline bath.

- The solution is easily reduced by hydrochloric acid and stannous chloride in the cold . . . .
  - Oxazines free from sulphur . . . . . . — $N\!\!<^{R'}_{R}\!\!>O,\ R=N\!\!\equiv$ — *e. g.,* Nile Blue.
  - Thiazines (contain sulphur . . . . . . — $N\!\!<^{R'}_{R}\!\!>S,\ R=N\!\!\equiv$ — *e. g.,* Methylene Blue.

- The solution is only reduced with difficulty and frequently imperfectly. It requires to be warmed, and an excess of hydrochloric acid and stannous chloride . . . .
  - Indulines.—Blue color with concentrated sulphuric acid giving a blue solution on dilution with water* — $N\!\!<^{R'}_{R}\!\!>N,\ R=N\!\!\equiv$ — Spirit-soluble Induline.
  - Safranines.—Green color with sulphuric acid turning blue and then violet on dilution . . . . — $N\!\!<^{R}_{R}\!\!>N:$ — Safranine T. extra.

Colored.—The color is not extracted by acetic acid. Neutral Dyestuffs.—Insoluble in water, soluble in alcohol; dye the fibre from an indigo vat.

- Blue dyestuffs affected by warm hydrochloric acid . . . .
  - Indophenols — $N\!\!<^{R}_{R}\!\!=O$ — Indophenol.
- Red or blue dyestuffs unchanged by hydrochloric acid; give isatin with nitric acid . . . .
  - Indogenides — $HN\!\!<^{R}_{}\!\!C\!\!<^{CO}_{:}$ — Indigotine.

Colorless, acetic acid does not extract anything. Acid Dyestuffs.—Soluble in water, dyeing wool from an acid bath.

- *Unsulphonated.*—Soluble in ether in presence of acetic acid . . . .
  - Oxazones — $N\!\!<^{R}_{R}\!\!>O,\ R=O$ — Fluorescent Blue, Orcein.
- *Sulphonated.*—Not soluble in ether . . . .
  - Easily reduced by stannous chloride and hydrochloric acid . . . . — Sulphonated Indogenides. Sulphonated Thiazines. — Indigocarmine. Thiocarmine R.
  - Reduced with difficulty by stannous chloride and hydrochloric acid . . . . — Sulphonated Indulines. — Water-soluble Nigrosine.

* The indulines and safranines differ in their basicity; the former can be liberated by ammonia and extracted by ether, whilst potash is necessary to obtain the safranine base.

TABLE D.

Group III.—Dyestuffs not Reduced by Stannous Chloride and Hydrochloric Acid having the Imidoquinone-carbonchromophore .N:R:C:

Description	Group	Example
Colorless, non-fluorescent, ethereal solution. The solution in acetic acid is non-fluorescent. The aqueous solution is decolorized by potash, and decomposed by hydrochloric acid	*Auramines*	e. g. Auramine O.
Colorless, greenish, fluorescent, ethereal solution. The aqueous solution is precipitated by potash, and only slightly changed by hydrochloric acid. Nitric acid colors it red	*Acridines*	Phosphine.
Colorless or colored non-fluorescent ethereal solution. The acetic acid extract is reddish-violet, blue, and green, without fluorescence. The aqueous solution is generally decolorized by potash on warming, and is turned yellow by hydrochloric acid (with the exception of the phenylated rosanilines)	*Rosanilines* (unsulphonated).	Magenta.
The ethereal solution is colorless, and does not fluoresce. The solution in acetic acid is pink and fluorescent. The aqueous solution is decolorized by potash	*Pyronines* (direct cotton dyestuffs are turned yellow by hydrochloric acid) . . .	Pyronine G.
	Rhodamines (unsulphonated) are unaffected by hydrochloric acid) . . .	Rhodamine S.
The ethereal solution is yellow, and does not fluoresce. The alcoholic solution is yellow and non-fluorescent, and is unaltered by aqueous acids or alkalies	*Quinophthalenes** (unsulphonated)	Spirit soluble Quinoline yellow.
Yellow dyestuffs soluble in water, without fluorescence, unchanged by aqueous acids or alkalies . .	*Sulphonated Quinophthalenes.*	Water soluble Quinoline yellow.
Water soluble dyestuffs, reddish-violet, blue, or green, generally decolorized by potash lye, little affected by hydrochloric acid	*Sulphonated Rosanilines.*	Magenta S.
Red or violet dyestuffs giving fluorescent aqueous solutions not affected by potash, or only slightly.	*Sulphonated Rhodamines.*	Violamine R.
Brownish-yellow or orange dyestuffs giving more or less fluorescent aqueous solutions, dyeing silk, wool, and cotton directly	*Thiazols.†*	Primuline.

The aqueous dye-stuff solution is boiled with bleached cotton. — *The cotton is not dyed.* / *The cotton is dyed.*

Colored or colorless solution. The color is extracted by 5 per cent. acetic acid. *Basic Dyestuffs.* Dye wool from an alkaline (NH₃) bath . . . .

The color is not extracted by acetic acid from the colored ethereal solution. *Neutral Dyestuffs.* Insoluble in water; soluble in alcohol . . . . .

The ethereal solution is colorless; acetic acid does not extract anything. *Acid dyestuffs.* All soluble in water, and dye wool from an acid (HCl) bath . . . .

The aqueous or alcoholic solution of the dyestuff is treated with KOH, and then extracted with ether.

*The quinoline dyestuffs Berberine and Flavaniline have no definite chromophore, and are intermediate between the auramines and acridines.

† The thiazol dyestuffs are generally sulphonated, with the exception of Thioflavine T, which, although soluble in ether, dyes wool from an alkaline bath

TABLE E.

Group IV.—Dyestuffs not reduced by Stannous Chloride and Hydrochloric Acid having the Oxyquinone-carbonchromophore O : R : C:

The alcoholic solution of the dyestuffs treated with a few drops of a dilute (1:1000) solution of ferric chloride.						Class	Example
Remains unchanged. Non-amidated triphenyl-methane dyestuffs, generally soluble in water, dyeing wool directly.	The dyestuff is dissolved or suspended in boiling water.	It does not dye wool directly. Generally insoluble in water, soluble in alcohol without fluorescence	Usually decolorized (with decomposition) especially on warming.	$C{<}^{R'}_{R''}$, $R = O$		*Aurines.*	Aurin.
		Dyes wool directly. Generally soluble in water and alcohol to fluorescent solutions	Gives an intense yellow without decomposition.	$C{<}^{R''}_{R}$ $R > 0$, $R = 0$		*Phthaleïnes.*	Eosin.
Turns green or olive green. Oxy-ketone dyestuffs, generally insoluble in water, dye fibres in-directly.	The original dyestuff is treated with 1 per cent. KOH.	Dissolves with a yellow or reddish-yellow color, *Monoketones*.	The alkaline solution is treated with an excess of hydrochloric acid.	$R{-}CO{-}R$		*Benzo-phenones.*	Alizarin Yellow A.
				$CO{<}^{R}_{}$ $C : C{<}^{O}$		*Flavones.*	Quercetin.
		Dissolves with a red, reddish violet, blue, or green color. *Diketones* (Quinones).	The alkaline solution is acidified with acetic acid. The free acid is precipitated. Generally soluble in ether, and dyeing the fibre indirectly.	$CO{<}^{R}_{R'}{>}CO$		*Anthra-quinones* (unsul-phonated).	Alizarin.
			The dyestuff acid remains in solution, is insoluble in ether and dyes wool directly.			*Anthra-quinones.* (sul-phonated).	Alizarin Red S.

By means of the preceding tables the group to which a dyestuff belongs may be discovered, and it may be further identified by recourse to a table of reactions for the particular group in question.

The various phthaleïns may be recognized by boiling the solution of dyestuff with potash and zinc-dust, and examining the filtrate, after neutralization with acetic acid, for bromine and iodine. Or the halogen may be determined by igniting the dyestuff with lime, dissolving in nitric acid, and examining the solution.

Thiazines may be distinguished from oxazines by detecting the presence of sulphur by fusing the dye with potassium nitrate, and testing the melt for sulphuric acid.

If the dyestuff has been reduced by stannous chloride, the reduction product may be further examined after removing the tin with hydrogen sulphide. Azo-dyestuffs on reduction give at least two primary amines, which can often be separated by means of ether. The reduced solution, after removing the tin with hydrogen sulphide, is treated with caustic potash and shaken with ether. The non-sulphonated amine will dissolve in the ether, leaving the sulphonated amine in the aqueous layer. The latter may frequently be further identified by observing the characteristic azo-compounds formed with certain diazo-derivatives. The presence of a para-diamine is recognized by the thiazine reaction, which is a treatment of the solution freed from tin with ferric chloride and hydrochloric acid in the presence of hydrogen sulphide. In non-amido-dyestuffs this reaction also affords a method of distinguishing between mono- and disazo-dyestuffs, and it is also possible to decide whether a sulphonic acid group is in the side or middle ring, since in the former case a thiazine is formed, which in the presence of caustic potash can be extracted with ether, whereas a sulphonated thiazine remains in the aqueous solution.

For the separation of mixed dyestuffs, Rota suggests an extraction with ether. For instance, it is possible to separate basic from acid dyestuffs by adding a 20 per cent. solution of caustic potash to the aqueous solution of the coloring matter and shaking with three times the volume of ether; the free bases will dissolve in the ether and leave the acids in the aqueous layer. The latter solution is neutralized with acetic acid and subsequently examined. The ethereal solution is washed with slightly alkaline water and then shaken with one-third of its volume of a five per cent. solution of acetic acid; the acid layer on evaporation leaves the dyestuff as a residue. Some dyestuffs are not extracted by the acetic acid, in

which case they are obtained by evaporation of the ethereal solution.

The acid coloring matters may often be separated by successive extractions with ether, by means of which they are separated into three groups:

(1) Those extracted by ether in the presence of one per cent. acetic acid solution.

(2) Those extracted by ether in the presence of hydrochloric or sulphuric acid.

(3) Those insoluble in ether.

By treating the ethereal solutions with water and dilute ammonia, a further separation can often be made (picric acid from Martius' yellow).

At times, when a separation cannot be effected by means of ether, it is possible to do so with wool. In such cases an aqueous solution (1:1000) of the dyestuff should be made alkaline with a few drops of ammonia and boiled with wool as long as the fibre is dyed. The latter is then washed with hot ammonia water, with pure water, and finally extracted with a five per cent. solution of hot acetic acid. On evaporation of this extract the basic coloring matters are left, and can be further examined. In the separation of acid coloring matters, an aqueous solution (1:1000) of the dyestuff should be acidified with a few drops of hydrochloric acid and boiled with wool as long as any color is extracted. The dyed wool is washed with acidulated water, then with pure water, and finally extracted with a five per cent. solution of ammonia. On expelling the ammonia by boiling the color is obtained in a neutral solution, and by treating wool with this solution a separation of some dyestuffs may be effected.

Other separations may be brought about by dyeing wool in a neutral, or in a strongly acid bath. Cotton may also be employed for separating the direct cotton colors from the indirect.

When a doubt exists as to the identity of a coloring matter, it is often of service to dye some fibre with it, when its behavior in an acid and alkaline bath, with and without mordants, and the color and reactions of the material will render recognition certain and easy.

Absorption-Spectra of Coloring Matters.

A valuable aid to the recognition of many coloring matters consists in the observation of the *absorption-spectrum*. For this pur-

pose a pocket spectroscope will often suffice, but it is far better to employ a m i c r o - s p e c t r o s c o p e, furnished with a proper comparison-stage and reflecting prism, so as to allow of the spectrum of the coloring matter under examination being viewed in juxtaposition with the spectra of standard specimens of known origin.

In comparing the standard liquid with the sample, it is necessary to regulate the light, so that neither spectrum shall suffer from the excess of illumination.   This may be done very effectually in the case of an object placed on the stage by the ordinary diaphragm attached to the microscope.   The comparison-stage should be furnished with a slit, giving a means of regulating the intensity of the light falling upon the comparison-prism.   In using the micro-spectroscope, it is usual to employ the coloring matters in the state of solution, and it is not desirable to use too high a dispersive power, as in that case the absorption-bands are apt to be imperfectly defined.   The nature of the solvent is by no means an unimportant factor in the results obtained, H. C. S o r b y having found that the position of the absorption-bands was in certain cases sensibly affected by the nature of the solvent employed. When possible, it is always desirable to use aqueous solutions. The liquid to be examined with the micro-spectroscope is most conveniently placed in a small cell made by cementing a piece of barometer-tube (half an inch to an inch in length) to a glass microscope-slide by means of purified gutta-percha.   The cement is not acted on by water, alcohol, or acid or alkaline solutions.   The tube-cell being filled with the liquid, is covered with a thin piece of glass (microscope-cover).   This is not absolutely necessary unless some change is anticipated from the action of the air on the contents of the cell, but the precaution adds to the perfection of the definition.   In recording the results of a micro-spectroscopical examination, Sorby has suggested the use of an *interference-spectrum*, which divides the visible spectrum into twelve equal parts. With such an arrangement the sodium line D comes very accurately at $3\frac{1}{2}$, that is to say, in the middle of the fourth light-space; the bands being shaded off gradually on each side, so that the shaded portions are about equal to the intermediate bright spaces. On this scale, the positions of the principal lines of the solar spectrum are about as follows:—

A	B	C	D	E	b	F	G
$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{3}{8}$	$3\frac{1}{2}$	$5\frac{11}{16}$	$6\frac{3}{16}$	$7\frac{1}{2}$	$10\frac{5}{8}$

In using the micro-spectroscope it is desirable to perform the operations and to subject the coloring matter to the action of reagents as much as possible in the very tube-cell used for the observation of the absorption-spectrum.

In working with the micro-spectroscope it is very important to employ a strength of solution which will allow of the absorption-bands being well defined, and yet permit of as much light passing as is compatible with distinct absorption. The proper strength to use can only be ascertained by experiment in each case, the most convenient plan being to employ a concentrated solution first of all, and then to dilute it with an appropriate solvent until the absorption-bands become weak, noting the spectrum after each change in concentration. Solutions should be kept in small test-tubes, hermetically sealed and filled as completely as possible with the liquids; but even under such conditions many coloring matters, especially those derived from plants, undergo profound change. Hence it is never safe to compare a recently prepared solution of a coloring matter with one which has been kept some time, unless it has been distinctly ascertained by previous experience that it is not liable to suffer change by long keeping. In employing the method as a means of differentiating colors it is highly important to compare the results with those produced by the pure coloring matters.[2]

The absorption-spectrum of a liquid containing two distinct coloring matters not having any chemical action on each other is identical with that which will be produced if the light traverse solutions of the two coloring matters in succession.[3] By employ-

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[1] The solid reagents should be employed in the form of coarse powder or small grains, which can be added to the solution in the tube of the cell by means of a stout platinum wire, hammered out into a spatular form at one end. The reagent is best mixed with the liquid by means of a small platinum wire, of which the flattened-out part is bent up at right angles so as to form a miniature hoe. By the vertical motion of this in the cell very speedy solution and admixture of the reagent are obtained.

[2] A large number of observations, together with valuable hints in manipulation, and an attempt at a systematic qualitative discrimination of animal and vegetable coloring matters by the micro-spectroscope, have been published by H. C. S o r b y (*Proceedings of the Royal Society*, No. 92, 1867).

[3] The well-known production of green by the mixture of blue and yellow is due to this cause. All yellow solutions transmit (and all yellow pigments reflect) the greater part of the red, yellow, and green light of the spectrum, while absorbing the blue and violet. Most blue liquids (and pigments) absorb the green rays

ing a reagent which will destroy or modify one of the colors in a
mixed solution without affecting the other, most valuable informa-
tion may be obtained, and in researches on unknown coloring mat-
ters evidence is often thus afforded of the complex nature of the
substance under observation.

P. S c h o o p (*Jour. Soc. Dyers*, &c., ii. 71) has described a means
by which the absorption-spectrum of a coloring matter may be ap-
plied to its quantitative determination. G i r a r d and P a b s t
(*Compt. Rend.*, ci. 156) have described and given drawings of sev-
eral coal-tar dyes likely to be used for adulterating wines and
syrups.   In some cases they can be extracted and separated from
the natural coloring matters by agitating the acidulated liquid with
amylic alcohol.

In the case of dyed fibres the absorption-spectrum of the color-
ing matter may be conveniently examined by stretching a thread
of the yarn or a very thin strip of the woven fabric across a black-
ened card or other black surface.   The strip, which is used in place
of a slit, is strongly illuminated, preferably by direct sunlight, and
observed by a spectroscope with a widely-opened slit, and the tele-
scope focussed on the card.   In this manner very useful results are
sometimes obtainable.

F o r m a n e k (*Zeits. Nahr- und Genussmittel*, 1899, 206), in his
spectroscopic investigations on dyestuffs, has found that the bands
of some dyestuffs in the same solvent are very close together; that
some dyestuffs do not possess any absorption-bands at all; and, in
cases where the dispersion is small, the absorption-bands of some
dyestuffs are superposed.   In order to obviate these difficulties he
examined dyestuffs in different solutions, by which the positions of
the bands were altered, or the same effect was produced by adding
acids or alkalies.

very imperfectly, and it is only such impure blues which produce greens on ad-
mixture with yellows.   If the light which has traversed such a blue solution,
e. g., indigo-extract (or which is reflected from such a blue pigment) be trans-
mitted through a yellow liquid (*e. g.*, picric acid, or an ammoniacal solution of
potassium chromate), the green portion of the spectrum will be almost the only
part which survives the double absorption, and hence the light transmitted ap-
pears green.

Fluorescence of Coloring Matters.[1]

Many coloring matters, *e. g.*, some of the eosins, magdala-red, purpurin, turmeric, resorcin-blue, &c., exhibit characteristic *fluorescence.* It is absolutely necessary that the liquid to be observed should be *perfectly clear*, as the presence of minute suspended particles often causes the production of a spurious fluorescence, which may lead to very erroneous conclusions. As a rule, the phenomenon of fluorescence may be observed by filling a small test-tube with the fluorescent liquid, holding it in a vertical position before a window, and observing the liquid from above against a dark background. Another plan is to make a thick streak of the liquid on a piece of polished jet or black marble or on a glass plate smoked at the back, and to place the streaked surface in front of, and at right angles to, a well-lighted window. In this manner very faint fluorescence may be detected.

In some cases the following method of observing fluorescence may be advantageously employed. A cell is made by cementing a piece of barometer-tube, about $\frac{3}{4}$ inch in length and having an internal diameter of $\frac{1}{8}$ inch. to a glass microscope-slide, by means of black sealing-wax. The open end of the cell must be well polished. On introducing a clear solution of any fluorescent substance, covering the cell with a piece of thin glass, placing the slide on the stage of the microscope, illuminating the tube-cell at the side by means of strong daylight, and looking down and observing the cell longitudinally by a low microscopic power, the liquid will appear more or less turbid, and of a color dependent on the nature of the substance in solution. If no fluorescent body be present the field will appear perfectly black, as no light is reflected from the apparatus or the liquid. When desired, the *spectrum* of the fluorescent light can be observed by the micro-spectroscope. In some instances the spectrum thus obtained shows remarkable and characteristic bands.

On the fibre the fluorescence of a dye is best shown by silk. Wool shows it sometimes, but on cotton the fluoresence can rarely be observed, owing to the rough character of the fibre.

[1] R. M e y e r (*Ber.* xxxi. 510) attempts to show that the fluorescence in some groups of organic compounds, like their color, is dependent on the presence in the molecule of certain groups of atoms, to which he proposes to give the name ''Fluorspore.'' This group is either a pyrone ring situated between more complex nuclei or the phthalic residue (anthracene derivatives and bodies containing nitrogen and sulphur being excepted).

Examination of Commercial Coloring Matters.

Dyes derived from coal-tar are usually definite chemical compounds, and hence when pure any particular dye should be of constant quality. The practice of mixing inert matters with coal-tar dyes ostensibly to bring the colors to a definite standard of strength, but possibly with the additional object of direct adulteration, is unfortunately very common. In some cases, especially where the dyes are intended for exportation, the "standard" of strength is as low as $2\frac{1}{2}$ per cent. of actual coloring matter, and in other cases, if not carried so far, adulteration is so generally practiced that the pure coloring matters are almost unknown commercially (*Jour. Soc. Dyers, &c.*, iv. 70).

Among the adulterants most largely used are common salt, sulphate of sodium, and dextrin. Sulphate of magnesium is also employed, as also oxalic acid and certain oxalates, sugar, glucose, starch, &c. J. J. H u m m e l has described a sample of spurious magenta, consisting of crystals of acid oxalate of potassium, coated over with real magenta by steeping them in an alcoholic solution of the dye. Bronze-powder has been employed for adulterating certain aniline dyes.

Excess of water is very common in paste-dyes. The water itself may be determined by drying a known weight at 100° and observing the loss, but it must not be assumed that the residue represents the true coloring matter of the sample. The dry residue should be macerated with warm water in a mortar, and the solution filtered. The insoluble matter is then again weighed, or the dissolved matter is determined by evaporating an aliquot part of the solution, when a residue may be obtained, consisting of common salt, dextrin, glucose, glycerin, etc.

The presence of *mineral matters* generally may be detected and determined by burning a known weight of the sample and weighing the ash, but it must be remembered that metallic oxides and alkali-metal salts are left on the ignition of many pure dyes. This will be the case with sulphonated dyes, double zinc salts, the salts of acid coloring matters, and many others.

Common salt is so commonly employed for salting out coal-tar dyes from their solutions, that its presence in moderate amount in non-crystalline coloring matters must not be mistaken for an intentional addition with a view of increasing the weight. The direct application of silver nitrate to the solution must not be relied on for the detection of common salt unless the dye is such as will not

contain the coloring matter in the form of a hydrochloride of the base, or yield an insoluble silver salt; but any chloride found in the ash left on igniting the sample probably existed as common salt, which usually can be recognized in the ash by its taste.   The eosins leave chlorides, bromides, or iodides on ignition; but if the aqueous solution of the coloring matter be acidulated with dilute sulphuric acid and agitated with ether, the dye will pass into the ethereal layer, and after repeating the process till extraction is complete, the aqueous layer may be at once tested for chlorides by adding silver nitrate.

The presence of *sulphate of sodium* in the ash does not prove the existence of that salt as an adulterant of the original coloring matter, since sulphonated dyes usually leave a sulphate or sulphite of alkali-metal on ignition.   The presence of a sulphate may be detected by the addition of barium chloride, to the acidulated solution of the original sample, but the precipitate obtained often consists wholly or largely of the barium salt of the sulphonated dye. On filtering, and treating the precipitate with ammonium carbonate, the sulphonate will be dissolved with formation of barium carbonate, and on then washing the residue and treating it with dilute hydrochloric acid any barium sulphate will be left undissolved. Sodium sulphate is often present in the azo-dyes, and may be detected by saturating the aqueous solution with chemically pure chloride of sodium, when the sulphonated coloring matter will be precipitated, and the sulphate can be detected by adding barium chloride to the diluted and acidified filtrate.   Sodium sulphate may frequently be detected, especially if present in any considerable amount, by carefully dissolving the dyestuff in strong alcohol, when the sodium sulphate will be left as a white residue, which may be dissolved in water and tested with barium chloride.

The presence of magnesium in quantity in the solution or ash of a dye almost invariably indicates adulteration with *magnesium sulphate*.

Eosin dyes sometimes contain *carbonates of alkali-metals*, which will be detected by the evolution of carbon dioxide on acidifying.

Dextrin is usually recognizable by its odor on dissolving the dye in warm water, or on heating it in a test-tube.   Where it is desired to ascertain the amount, from 1 to 2 grammes of the coloring matter should be washed with strong alcohol, the residue dissolved in the smallest possible quantity of water, and the solution filtered into a tared beaker containing a weighed glass rod.   Alcohol is

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then gradually added as long as a precipitate is formed, whereby the dextrin is separated in flocks, which on stirring become attached to the sides of the beaker. The liquid is poured off, and the beaker and glass rod rinsed with rectified spirit, dried at 100° or slightly higher temperature, and weighed.

Sugar is not infrequently employed as an adulterant of dyes. Crystallized magenta is often thus sophisticated.

On spreading out such a sample on a piece of white paper placed in a strong light, the large fragments may be recognized by their edges being less deeply tinted than the genuine crystals of the dye. When removed and cautiously washed with strong alcohol, the sugar fragments become nearly colorless, and may be identified by the odor of caramel produced on heating. The amount of sugar present may be ascertained in many cases with approximate accuracy by treating a known weight of the sample with absolute alcohol saturated with sugar, or with alcohol mixed with a little ether. A method of determining sugar in magenta and other basic dyes consists in precipitating the hot aqueous solution by picric acid. The filtered liquid is treated with basic acetate of lead, again filtered, the lead in the filtrate removed by sulphuretted hydrogen or sulphurous acid, and the sugar estimated polarimetrically, or inverted and determined by Fehling's solution.

Starch is left insoluble on treating the sample with cold water or alcohol, and may be readily recognized in the residue by its microscopical characters and the blue coloration produced with iodine.

Arsenic is sometimes met with as an impurity in magenta and other aniline dyes, though the frequency of its occurrence has been exaggerated. It may be detected and determined as described on page 283.

Antimony and other poisonous metals are sometimes employed for mordanting dyes, and irritation of the skin and other ill effects have been attributed to their presence. The subject has been discussed at length by J. R. Ashwell and H. Forth (*Jour. Soc. Chem. Ind.*, v. 226, 301).

Foreign coloring matters may often be recognized by a judicious treatment with solvents, or more systematically as described in the preceding pages.

A valuable mode of ascertaining the actual percentage of coloring matter in a coal-tar dye consists in comparing its oxidizing power with that of an equally concentrated solution of some pure

dye of the same nature, used under precisely similar conditions. For this purpose two equal quantities of solution of sodium hydrosulphite ($NaHSO_2$) should be introduced into small flasks containing a little petroleum burning-oil (kerosene). If magenta is the color to be examined, a solution of rosaniline of known strength is then run in from a burette, while the flask is immersed in boiling water. The decolorization is instantaneous, and the process is at an end when a permanent pink tint is obtained. An equal volume of the hydrosulphite is then treated in an exactly similar manner with the solution of the sample to be tested, when the volume run in from the burette, compared with the measure of pure rosaniline solution previously employed, gives the requisite data for calculating the purity of the sample. When it is merely desired to compare the *relative* purity of two dyes, one of them is employed instead of the standard sample.

According to A. S t a m m (*Jour. Chem. Soc.*, xxvi. 1263) 1 molecule of any aniline dye reduces the same volume of hydrosulphite as 2 molecules of ammonio-cupric sulphate, and hence the method may be employed for ascertaining the molecular weights of aniline-derivatives. Hofmann's violet and Paris violet give absolutely identical results, and Paris green requires a volume of hydrosulphite closely corresponding to the formula $C_{20}H_{17}(CH_3)_5N_3Cl_2 + H_2O$.

Another useful quantitative method of examining many basic dyes consists in precipitating the solution by a standard solution of picric acid, in the manner described on page 117.

Night blue may also be employed for the purpose of ascertaining the value of certain colors. R a w s on (*Jour. Soc. Dyers, &c.*, 1888–82) describes this method as applied to naphthol yellow. A standard solution of night blue is prepared by dissolving 10 grammes of the dyestuff in 50 c.c. of glacial acetic acid, and diluting to 1 litre with water. Solutions of samples of naphthol yellow S are prepared containing 1 gramme per litre. 10 c.c. of the solution of night blue are placed in a small flask and the solution of naphthol yellow is run in from a burette until a portion of the liquid on filtration shows a yellow tint. The value of the samples examined will be in inverse proportion to the number of c.c. required to precipitate 10 c.c. of night blue solution. The latter may be standardized by the use of pure recrystallized naphthol yellow S, and the percentage of pure dyestuff in the sample may thus be found. 1 gram of commercial night blue will precipitate about

0.25 gram of pure dry naphthol yellow S ; it would thus appear that two molecules of night blue combine with one molecule of naphthol yellow S.

This method is applicable in general to the valuation of azo-dyes; but care should be observed that in the comparison of two dyestuffs they should possess a similar constitution. But samples of the same dyestuff can be compared by this process with great precision.

A simple and useful means of examining coloring matters is by making a solution and diluting it with water or alcohol (as the case may require) until the depth of color is identical with that of a solution of known strength made from a standard specimen. The operation is conducted in a manner similar to the Nessler test for ammonia in water, or the colorimetric determination of carbon in steel.

One of the best methods of assaying aniline dyes, both for purity of tone and amount of coloring matter, is to compare the dyeing powers of the sample with those of a specimen of known purity. As a rule, from 1 to 3 grammes of each specimen should be dissolved in a litre of distilled water. Equal weights of unstoved white woolen yarn are suspended in each solution. The liquids are immersed in the same water-bath, which is heated gradually to 80° C. After an interval of one hour from the commencement, the temperature may be increased till the water boils, and after another half hour the swatches of wool may be removed, rinsed with water, and their tints compared. When the wool is not dyed to an extent approaching saturation, it is easy to compare the relative depths of the tints. By employing 1 gramme of the standard, and several quantities, varying from 1 to 2 grammes, of the sample to be compared, it is easy to arrive at their relative dyeing powers. As a rule, water only is necessary, but some dyes are best tested in a slightly acid solution. In testing soluble blues, the wool should be heated to boiling in a dilute solution of the dye to which borax has been added, and the swatches then removed, rinsed with water, and the color developed by immersion in dilute acid.[1]

Another method of operating is to dissolve 0.5 gramme of the coloring matter in warm alcohol, and dilute the solution to 50 c.c., so as to obtain a 1 per cent. solution of the dye. Some water is heated nearly to boiling in a porcelain basin, and 1 gramme of

[1] For description of a suitable dyeing apparatus, see page 248.

fine white wool immersed in it till thoroughly wet. The wool is then removed, and 1 or 2 c.c. of the dye solution added, after which the wool is put back and the liquid heated for ten minutes. Should the whole of the color be taken up, the wool is again removed, another addition to the dye solution made, the dyeing repeated, and so on till the wool is saturated The volumes of dye-solutions decolorized by the wool in a series of experiments will be inversely as the purity of the samples of dye examined.

Some dyes, such as picric acid, cannot be completely withdrawn from their solutions, and in such cases the method is not applicable. In many instances, mixtures of dyes can be detected by dyeing successive small portions of wool in the same bath, when the color fixed will often be notably different in tint, owing to the varying affinity of different dyes for the fibre.

Special methods of applying miniature dye-tests to certain coloring matters are described in the preceding sections.

Examination of Dyed Fibres.

W. S t e i n (*Dingl. polyt. Jour.*, ccx. 245) gives the following direction for testing the *fastness of dyes* on colored fibres. They must be received with caution so far as the newer coal-tar dyes are concerned:—*Red* dyes should not color lime-water or soap solution when dyed therewith, and the fabrics themselves should not be altered in color by this treatment. A negative result when thus treated indicates the absence of brazil-wood, archil, safflower, sandal-wood, and many coal-tar dyes. *Violet* dyes may be considered unstable if they yield any considerable quantity of their color when boiled with a mixture of equal parts of rectified spirit and water, and left to stand for fifteen minutes; or if, on boiling with dilute hydrochloric acid, they change in color to brown or brownish-red, and color the liquid red. Fast *blue* dyes should not give up any coloring matter when boiled with alcohol or warmed with a mixture of hydrochloric acid with water and alcohol. *Green* dyes when boiled with alcohol should not color the liquid either blue, green, or yellow; and hot hydrochloric acid should not acquire a red or a blue color from green fabrics. The fastest *yellow* is madder-yellow, which yields no color to either water, alcohol, or lime-water used in succession. *Orange* dyes should not be dissolved from the fibre by boiling water or warm alcohol. *Brown* dyes may be considered unstable if they color boiling water red, or give a yellow color to alcohol when left in contact with it. If a

black fibre, when boiled with dilute hydrochloric acid, colors the liquid merely yellow, it may be considered fast, as, for instance, tannin-black; and if the color of a fresh portion is changed to brown when boiled with a solution of carbonate of sodium, there is probably only tannin-black present. If the fibre thus treated remains black or turns blue, it is probably bottomed with indigo under the tannin-black; while if the fabric colors hot dilute hydrochloric acid red, and is itself turned brown by the treatment, it is dyed with logwood-black, and may be considered unstable; but if when boiled with acid the stuff becomes blue and colors the liquid red, it is logwood-black bottomed with indigo, and will have a certain degree of stability.

The power of a dyed color to withstand the action of certain reagents either chemical or physical is of considerable importance in determining the suitability of a dyestuff for a particular purpose The *fastness* of colors has reference to their permanence against the action of *light, washing, fulling, acids, alkalies, stoving* (sulphur), *bleaching* (chlorine), *ironing* (calendering), *rubbing* and *perspiration.* The required degree of fastness of any color will of course depend on the use to which the dyed material is to be put; some goods requiring very fast dyes, whereas others do not. In order to determine the fastness of any dyestuff to the various agencies above enumerated, it will be necessary to make experimental tests on a piece of fabric dyed with coloring matter in question.

Light test.—A sample is exposed to the action of direct light for 10 days; it is best to arrange the sample in such a way that one-half is exposed while the other half is shielded. The exposure should be made as much as possible in direct sunlight, but protected from the atmosphere by glass. If an appreciable fading only has taken place in 10 days, the color is moderately fast; if very much faded it is fugitive.

Washing test.—This is carried out by scouring a small sample of the dyed material in a bath containing 10 to 15 grammes of neutral soap per litre at a temperature of 120° to 140° F. The sample should be immersed in the solution for 15 minutes, then washed and dried. If the color is abstracted from the fibre in any appreciable degree it cannot be considered fast to washing or scouring.

Fulling test.—A sample of the material is twisted together with white wool and cotton, and steeped in a soap bath similar to the above, only a small amount of soda ash (5 grammes per litre) is added. The sample should be squeezed and twisted with the

fingers in order to simulate the action of fulling. If the color bleeds into the white, the dye is not fast.

Acid test.—For woolen materials a sample should be soaked in a 10 per cent. solution of sulphuric acid at 140° F., after which it is washed and dried. For cotton fibres acetic acid at 100° F. should be used. The acid test also represents fastness to perspiration.

Alkali test.—A sample of the dyed material should be steeped for 10 minutes in a solution containing 10 grammes of soda ash per litre at 120°–140° F., washed and dried. This test is sometimes performed by sprinkling the material with milk of lime, allowing it to dry in and then brushing off. Fastness to alkali represents resistance to action of street dust, alkaline country air, etc.

Stoving test.—A sample of the dyed material is subjected to the action of sulphurous acid fumes for several hours.

Bleach test.—A sample of the dyed material is steeped for 10 minutes in a solution of bleaching powder at $\frac{1}{2}$° Tw.

Ironing test.—A sample of the dyed fabric should be slightly moistened, placed between two pieces of muslin, and pressed with a hot iron.

Hydrogen peroxide test.—Steep a sample of the dyed fabric for 1 hour in a cold solution of hydrogen peroxide (10 vols.). This represents the fastness of a dye to out-door atmospheric exposure.

Water test.—This is applied exclusively to silk; a sample of the dyed material is twisted with white silk and steeped for 12 hours in cold distilled water.

Rubbing test.—A piece of the dyed fabric should be vigorously rubbed on a white surface of paper or cloth.

Recognition of Dyes on Fibres.

The recognition of artificial coloring matters on fibres is tolerably simple when only one dye is present, especially if no mordant has been employed. But when two or more dyes have been used, either in conjunction or succession, as is very frequently the case, the problem becomes more complicated, and the difficulty is further increased when the natural coloring matters and the mordants generally accompanying their use have to be taken into account.

In many cases, the identification of a dye is greatly facilitated by a knowledge of the mordant employed. Where the mordant is inorganic, its nature is best ascertained by examining the ash

left on igniting the fibre.[1]　Organic mordants, such as tannin and albumin, are difficult to recognize in presence of coloring matters, and must be sought for by their special reactions.　Fibres dyed with coal-tar coloring matters usually leave but little ash on ignition, as they require no mordant on silk or wool, and on cotton are usually fixed by means of tannin.　On the other hand, alizarin and madder dyes leave an ash containing a notable quantity of alumina or oxide of iron; while the ash of fibres dyed with cochineal, brazil-wood, &c., will be found to contain either alumina or oxide of tin.　Logwood-black is mordanted with chromium and occasionally copper, while iron is a constituent of some blacks and violets, as also of prussian-blue.　Lead is found in chrome-yellow, and is the base of vermilionette.　Nickel is now employed for mordanting certain dyes, and antimony is also used.

The behavior of the principal coloring matters on the fibre has been to a great extent described in the special paragraphs relating to the different dyes.　Detailed and tabulated methods of examining dyed fabrics have been published by F o l (*Jour. Chem. Soc.*, xxviii. 193), S t e i n (*Zeits. Anal. Chem.*, ix., x.), J o f f r e (*Jour. Soc. Chem. Ind.*, i. 447, 496), and other writers.　R. M a r t i n o n (*Jour. Soc. Dyers*, iii. 124) has published a scheme for the detection of dyes on *silk*, and G. D o m m e r q u e (*Jour. Soc. Chem. Ind.*, viii. 216) a similar method for the recognition of dyes on wool.　A more general tabulation of reactions has been published by J. J. H u m m e l (*Dyeing of Textile Fabrics*), and this has been supplemented by R. L e p e t i t (*Jour. Soc. Dyers, &c.*, iv. 133).

K n e c h t and R a w s o n, and L e h n e and R u s t e r h o l z have also published very comprehensive tables.

EXAMINATION OF RED-DYED FIBRES.　The *red dyes* are very

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[1] Inorganic mordants may be tested for in the following manner:

Chromium :—Ash yellowish- or brownish-green ; on fusion with potassium chlorate a yellow mass is obtained, which if dissolved in water and acetic acid gives a yellow precipitate with lead acetate.

Iron :—Ash is reddish-brown in color; dissolved in hydrochloric acid it gives a blue precipitate with potassium ferro-cyanide.

Copper :—Dissolve the ash in hydrochloric acid, add slight excess of ammonia, and filter; a blue filtrate indicates copper; potassium ferrocyanide gives a reddish-brown precipitate.

Aluminium :—Ash is white; dissolved in hydrochloric acid, the addition of ammonia gives a white precipitate.

Tin :—Ash is white; may be reduced to metallic globules by heating on charcoal.

numerous and often difficult to identify, and hence the following hints may be found useful.

1. Boiling *alcohol* removes magenta, safranine, corallin, aurin, spirit eosins, archil, santal- and bar-wood, but does not greatly affect tissues dyed with red and claret azo-dyes, acid magenta, magdala-red, alizarin and madder-dyes, cochineal, safflower, brazil-wood, lac-dye, or kermes, and does not extract soluble eosins if well dyed. Purpurin is partially extracted, coloring the alcohol red. Magenta, safranine, and archil also color the alcohol red, and santal-wood yellowish-red, but the others form yellowish, brownish, or nearly colorless solutions. On evaporating the alcoholic solution to dryness, and treating the residue with strong sulphuric acid, magenta yields a yellow or brown solution, but safranine produces a fine green color, changing through various tints by gradual addition of water.

2. Magenta may be distinguished from archil-red and aurin by treating the fibre with *amylic alcohol*. This is colored bluish-red by magenta, pink or violet by archil, and yellow by aurin. On shaking the colored amylic alcohol with ammonia, it is decolorized if the dye be magenta, but the color will be unchanged if archil, and turned bluish-red if aurin be the coloring matter present.

3. *Ether* removes corallin, aurin, and eosin more or less perfectly. Tissues dyed with Turkey-red acquire a dull cherry-red color, and the ether leaves a brilliant scarlet fat on evaporation. This, when boiled with caustic soda, yields a purplish-blue solution, from which acids precipitate orange-colored flakes of alizarin.

4. By boiling with *ammonia*, corallin, aurin, and the eosins are usually dissolved from the tissue, the liquid being colored pink or red.[1] On removing the tissue, and agitating the liquid with ether and an acid, the coloring matters are extracted from the aqueous liquid, and may be detected in the ethereal solution by separating it, and evaporating to dryness or agitating with ammonia. Safflower colors ammonia salmon-tint. On the azo-reds ammonia

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[1] When boiled with concentrated solution of caustic potash (20–40 per cent.), Eosin G gives an orange-red solution, which on continued boiling becomes purple, and finally blue, with a strong green fluorescence. Neither the color nor the fluorescence is changed by dilution. Eosin B, when similarly treated, gives a bluish-violet solution, with pale green fluorescence. On dilution, the liquid becomes reddish-purple. Eosin BN, when boiled with potash, gives eventually an olive-green non-fluorescent solution.

usually has no action, and the same remark applies to alizarin and magdala red. Fibres dyed by magenta and acid magenta are decolorized, and safranine gives a pink solution. The vegetable coloring matters usually behave as with soda.

5. On moistening the fibre with a dilute solution of *caustic soda* (5 to 10 per cent.), the color due to rosaniline is very gradually destroyed. Safranine remains unchanged, but safflower is turned pale yellow, the original tint being restored by an acid. Cochineal gives a purple solution. Aurin, corallin, and eosin behave as with ammonia. From fibres dyed with brazil-wood caustic soda extracts much of the dye, cotton being almost decolorized, and the solution becoming bluish-red. Bar-wood and santal-wood give no color to the liquid, but the fibre becomes purplish. With archil the fibre becomes bluish-purple, and with magdala-red a dirty violet.

6. On treating the tissue with moderately strong *hydrochloric acid* (sp. gr. 1.11), magenta is turned brown or yellow, but the color is restored by washing with water. Hydrochloric acid does not change the color of fibres dyed with acid magenta, but the liquid acquires a faint bluish-red color. Safranine is unchanged by dilute acid, but with strong acid a blue color is produced, restored to red by washing with water. Turkey-red is unchanged. The azo-reds are usually (but not invariably) turned more or less violet, a colored liquid being extracted. Of the azo-dyes from benzidine, &c., fibres dyed with congo-red are turned blue-black by hydrochloric acid, and delta-purpurin, benzo-purpurin 11 B, and congo-corinth give similar reactions. With rhodamine the fibre is turned a dirty brick-red, without the liquid being colored. The original hue is restored by washing. The eosins are turned yellow or brownish-yellow. Tissue dyed with brazil-wood is turned bright orange by dilute acid, and corallin, aurin and cochineal yellow. Ammoniacal cochineal, however, is unchanged by dilute acid.

7. On boiling the tissue in an aqueous solution of aluminium sulphate the liquid will become reddish with most dyes, and in the case of madder-red or purpurin will show a green fluorescence. On adding an equal measure of acid sodium sulphite to the red liquid, the solution will be bleached if the dye be magenta, safranine, corallin, safflower, brazil-wood, or santal-wood, but not bleached if the color be due to archil, cochineal, lac-dye, or kermes.

8. On igniting the tissue, the red coal-tar dyes usually leave very little ash, as they require no mordant on silk and wool, and on cotton are usually fixed by means of tannin. On the other hand, madder red and pink leave an ash containing a notable quantity of alumina, and the ash of tissues dyed with cochineal or brazil-wood, or other dye-woods, will usually be found to contain either alumina or oxide of tin. Vermilionette is a lead compound of eosin, but its use is chiefly restricted to pigments.

RECOGNITION OF THE CONSTITUENT DYES OF COMPOUND SHADES.— The following hints, chiefly by G. Dommerque (*Jour. Soc. Chem. Ind.*, viii. 216), will be found of service for identifying the constituents of mixed dyes on wool.

Garnet Shades contain red as the predominating constituent. Bright garnets are a mixture of yellow and red. In examining them, moisten the fibre with hydrochloric acid. If turned yellow, the yellow constituent was Manchester yellow (dinitro-cresol), this being the only yellow which is dyed in a neutral bath, and which does not precipitate the salts of rosaniline. If on application of hydrochloric acid the shade becomes slightly bluer, the color is probably produced from acid-magenta and napthol-yellow or chrysoin; while if it turn violet acid-magenta and orange IV (or an allied orange or yellow azo-dye) are indicated. All bright garnet shades lose their red color when moistened with ammonia, yellow remaining. The rarely occurring shades produced with bordeaux and amaranth are not altered by ammonia, but become violet-blue or blue when touched with sulphuric acid.

Maroons and Compound-Red Shades are examined by moistening the fibre with ammonia. If it become green, the fibre was probably dyed with a mixture of acid-magenta and sulphonated indigo. If turned yellow, the same portion of fibre should be slightly washed and treated with hydrochloric acid, when if the yellow become violet, orange IV or other azo-orange or yellow is indicated; while if rendered slightly blue, chrysoin or naphthol-yellow is the probable yellow constituent. If the yellow color produced by ammonia remain unchanged on subsequent treatment with hydrochloric acid, the presence of acid-green, acid-violet, and acid-magenta is probable. If orange IV be also present, the fibre becomes reddish-violet with hydrochloric acid. If the color be unaffected, or simply rendered paler by treatment with ammonia, the dye may be either:—a mixture of an azo-red, indigo and orange IV, in which case it becomes slightly violet with hydro-

chloric acid (if this acid produces no change, chrysoïn is probably present); or logwood, becoming red with hydrochloric acid. If dyed with a mixture of logwood and orange IV, acid changes the color to violet-red or garnet.

Scarlets.—Cochineal-scarlets are turned violet by caustic alkalies, and the ash contains tin; alkalies turn artificial scarlets yellow.

Dark Blues and Purples.—Complete decolorization on moistening the fibre with ammonia points to a probable mixture of acid-green, acid-violet, and acid-magenta. If the red be removed from the fibre and the blue left, the latter is probably indigo and the former acid-magenta. If the shade become slightly pale the dye is probably a mixture of indigo and an azo-red, in which case the shade will not be appreciably changed on further testing the fibre with hydrochloric and sulphuric acid. Logwood will color the acid red, and the ash will contain chromium. In shades produced by mixtures of logwood, sulphonated indigo, and acid-magenta or an azo-red, the constituents are difficult to identify.

Dark Greens.—If only the yellow remain on moistening the tissue with ammonia, a mixture of acid-green and acid-violet with naphthol-yellow or picric acid may be suspected. Should the shade if changed become paler, the fibre is moistened with hydrochloric acid, when logwood will color the acid red. If the fibre become red or violet-red, and the ash contains chromium, the yellow constituent is probably fustic. If, on treatment with the acid, the yellow disappears and the blue remains, a mixture of indigo with picric acid or naphthol-yellow is probably present.

Olives, when moistened with ammonia, turn yellow if dyed with a mixture containing acid-green and acid-violet, and on treating the fibre with hydrochloric acid it will become garnet if the yellow constituent be orange IV, and yellow-brown if it be chrysoïn. Olives containing indigo become slightly bluer with ammonia.

Mode Colors are liable to contain a great variety of dyes, perhaps the most common being archil, archil-substitutes (azo-reds), azo-oranges, and acid-magenta.

Tables of Reactions of Dyed Fibres.

The following tables, by B. Martinon (*Jour. Soc. Dyers,* iii. 124), for the recognition of dyes on silk, are not so complete as some other schemes, but are more systematic, and involve the use of certain reagents, such as a solution of bleaching powder and nitrous acid, which are sometimes neglected. The reagents employed are:—

Caustic Soda Solution.—1 part in 10 of water.

Hydrochloric Acid.—Acid of 1.16 sp. gr. diluted with an equal volume of water.

Calcium Hypochlorite.—40 grms. of bleaching powder dissolved in 1 litre of water and the liquid filtered.

Nitrous Acid.—20 grms. of sodium nitrite and 15 grms. of sulphuric acid (sp. gr. 1.845) are respectively dissolved in 1 litre of water. Equal volumes of these solutions are mixed when required.

Potassium Cyanide.—50 grms. in 1 litre of water.

Nitric Acid.—Acid of 1.32 sp. gr., diluted with an equal volume of water.

Sodium Carbonate.—1 part of the salt in 10 parts of water.

From 10 to 15 c.c. of the required reagent should be placed in a porcelain dish, the silk to be tested immersed in it, and the change of color observed. After two or three minutes, the silk is taken out and well washed. Another portion of the silk should be simultaneously placed in clear water, in order that any change in color by the action of the reagent may be better observed. To ensure absolute certainty, it is also advisable to dye a piece of clean silk with the detected dye, and to repeat the experiments on this from the beginning.

G. D o m m e r q u e has published (*Jour. Soc. Chem. Ind.*, viii. 216) a systematic method of recognizing dyes on wool. In some cases different observers have given different reactions for the same dyestuff; and, on the whole, the reactions for dyes on the fibres is still in rather an unsatisfactory and uncertain condition, leaving much to be desired in this direction.

The tables of H u m m e l, L e p e t i t, K n e c h t and R a w s o n, and L e h n e already referred to, together constitute the most complete description of the reactions of dyes on fibres yet compiled, and as the present section would be imperfect if these reactions were omitted, they are given in a compilation with a few modifications from the above references in the following pages.

Yellow Dyes—on Silk.

No action.

NaOH

No action. HNO₃ { Green-yellow, then dirty green. On washing, slowly faint yellow . . . . Saffron.
{ Faint brown; on washing again yellow . . . . Quinoline Yellow.

Alters shade slightly { Alkaline liquid brownish-yellow, { HNO₃ and washing } No action . . . . Fustic and SnO₂.
with faint green fluorescence { Brownish-yellow } . . . Fustic and Al₂O₃.
The alkaline liquid is yellow. With HNO₃ silk becomes yellowish-brown Quercitron and SnO₂.

Brown-yellow { CaOCl₂ { Brown; with HNO₃ brownish-yellow . . . . . Sumac and Al₂O₃.
{ Brown; with HNO₃ chestnut-brown . . . . Alkanet.
Reddens somewhat. CaOCl₂ without action . . . . Heliochrysin.
Turns red and then decided brown; on washing again yellow. With HNO₃ more
yellow . . . . Nitro-alizarin.
Faint greenish-yellow. CaOCl₂ decolorizes. On washing remains a faint yellow color . Phosphine.
Pure yellow. CaOCl₂ bleaches silk slowly . . . . Chrysoïdine.

H₂O { Bleached on washing. CaOCl₂ without action . . . . Quercitron and Al₂O₃.
{ Bleached by washing, and remains brown-yellow. With CaOCl₂ silk becomes brown . Weld and Al₂O₃.
yellow { { Color does not return after washing . . . . Chrome Yellow.
Decolorizes { Color reappears { Na₂CO₃ without action . . . Auramine.
on washing { Na₂CO₃ decolorizes . . . . Flavin.
Reddens . . . { Reddish-brown . . . . . Aurantia.
{ No action . . . . . . Picric Acid.
Changes slowly into orange-yellow. With KCy { No action . . . . Naphthol Yellow S.
Scarlet . . . . Chrysamine.

Decolorizes or bleaches considerably

HCl {

Intense red. ICl colored violet-red. With water silk turns brownish-red, then again yellow . Orange IV.
Reddish-brown. NaOH { The silk becomes reddish-brown. HNO₂ without action . . . Turmeric.
{ The NaOH is colored orange. HNO₂ chestnut-brown . . Young Fustic.
Dark yellowish-brown color; on washing it remains a brownish-yellow. With NaOH chestnut-brown,
with CaOCl₂ orange . . . . Alkanet and Al₂O₃.
Reddish; with NaOH chestnut-brown. CaOCl₂ and HNO₂ without action . . . . Citronin.
Orange. NaOH faint brown. With CaOCl₂ color becomes slightly red . . . . Amidoazobenzene.
Orange; with NaOH scarlet. CaOCl₂ wood color. With HNO₂ reddish-brown . . . Chrysoïn.

ORANGE YELLOW DYES—ON SILK.

HCl {

Without action } NaOH { No action . . . . Turmeric.

action } Reddens and turns decided brown. HNO₂ without action . . . Nitroalizarin.

NaOH { Scarlet . . . . Orange I and II.

Scarlet, more or less } NaOH { Pure Yellow . . . . Orange III.
brownish

RED DYES.

HCl {

No action {

Turns somewhat brown . . . . Rocellin.

NaOH { Violet-red { HNO₂ { No action } HNO₃ { Brownish-red . . . Magdala Red.
                          No action }   Reddish-violet . . Archil substitute.

The silk becomes violet { Bleached and turned yellow. . . . . Archil.

Bluish-violet { NaOH { Scarlet. CaOCl₂ no action . . . . Congo Red.
                      Pale violet-red. CaOCl₂ decolorizes . . . . Safranine.

Reddish-violet. NaOH decolorizes . . . . Acid Magenta.

{ NaOH { Decolorizes slowly; silk remains faint rose-color, and becomes red on washing . . . Magenta.
        No action . . . . Benzopurpurin.
        Silk becomes lilac . . . . Ammoniacal Cochineal.

HCl {

Bright yellow [NaOH] [Violet-red] [CaOCl₂]

Na₂CO₃ { No action. Solution in boiling alcohol is fluorescent . . Eosin.
        The Na₂CO₃ becomes pale violet . . . . Erythrosin.

First violet, then slowly loses color . . . . Cochineal.

CaOCl₂ { No action. The Na₂CO₃ becomes violet . . . . Alizarin.

Silk decolorized; the soda solution is colored brownish-red . . . . Safrosin.

Silk more or less brownish-yellow { NaOH { No action { HNO₂ { No action . . . . Silk Scarlet.
                                                              Wood color. . . . Peonin.
                                          Silk black-brown . . . . Scarlet.
                                          Silk scarlet. HNO₂ slowly colors it yellow . . Red Woods.

Silk decolorized { NaOH { Silk reddish-violet { HNO₃ { Decolorizes . . . . Primrose.
                                                       Silk becomes cream-colored . . Bengal Red.
                          Silk gray . . . . Murexide.

BLUE DYES—ON SILK.

No action.

HCl

NaOH

Silk dirty green, the soda is colored yellow . . . . Indigo Carmine.

Silk at first dirty green, then loses color.
The alkaline solution gives a blue precipitate with HCl and ferric chloride . . . Prussian Blue.

$CaOCl_2$ { Silk de-colorized } HNO_3
  - Silk bluish-gray. . . . Spirit Blue.
  - Silk faint lilac . Alkali Blue.

Silk red, more or less of violet shade } $CaOCl_2$ { Silk de-colorized } HNO_3
On washing, it again turns blue
  - Silk Black-blue and then chestnut brown . . . Water Blue.
  - No action . . . . Azo-Blue.

Shade changes to red, but by washing again becomes blue. . . . . . . Induline.

$CaOCl_2$
  - Silk slowly becomes gray. With HNO_3 reddish-gray . . . . Basle Blue.
  - No action. With HNO_2 silk becomes green, with HNO_3 a dirty green . . . Methylene Blue.
  - Slowly decolorizes. With HNO_3 silk green, then cream-colored . Indigo.

No action
  - Pale chestnut-brown. With H_2O green, then greenish-blue . . . . Indophenol.
  - Reddish-brown. With H_2O blue . . . . Alizarin Blue.
  - Scarlet. With water it turns first violet, then blue . . . . . Resorcin Blue.
  - Green. With water blue color reappears instantly. . . . . . . Victoria Blue.

VIOLET DYES.

HCl

Blue, then bluish-gray and orange. Water again produces violet. NaOH reddens . . . Methyl Violet.

Blue. With water original color reappears. With NaOH blue . . . . . . Mauvein.

Reddish-brown . . . . Gallein.

GREEN DYES.

HCl

No action. Fibre contains Fe_2O_3 . . . . Resorcin Green.

Silk gray, HCl colored red-brown. On washing gray color remains . . . . Cœrulein.

Silk yellow. NaOH { Decolorizes. Silk remains unchanged on heating to 100° . . Malachite Green.

Silk yellow. NaOH { Decolorizes. On heating to 100° silk is colored violet . . Methyl Green.

Silk green-yellow. With NaOH brown-gray. On washing original color does not reappear . Aldehyde Green.

The following abbreviations are employed for the names of firms identified with the production of certain dyes:—

B.   Badische Anilin und Sodafabrik.

M.   Meister, Lucius, & Bruning (Höchst).

A.   Actiengesellschaft für Anilinfabrikation in Berlin.

D. H.   Durand & Huguenin (Basle).

B. S. S.   Brook, Simpson, & Spiller (London).

By. Farbenfabriken of Elberfeld Co., vorms, F. Baeyer & Co.

C.   Leopold Cassella & Co. (Frankfurt).

D.   Dahl & Co.

K.   Kalle & Co. (Biebrich).

L.   Farbwerke Mühlheim vorms. Leonhardt & Co.

N.   Noetzel & Co. (Greisheim).

H.   Read Holliday & Sons (Huddersfield).

O.   K. Oehler (Offenbach).

Sch.   Schoellkopff Aniline Co. (Buffalo).

I.   Société pour l'Industrie Chimique (Basle).

Mo.   Gilliard, Monnet, & Cartier (Lyons).

P.   Société Anonyme des Matières Colorantes de St. Denis (Paris).

G.   Geigy & Co.

Cl.   Clayton Aniline Works (Manchester).

Various other abbreviations are employed with the object of saving space, but they will probably be readily intelligible without special description.

The reagents applied are concentrated hydrochloric acid (sp. gr. 1.11), concentrated sulphuric acid, caustic soda (10 per cent. solution), strong ammonia, a hydrochloric acid solution of stannous chloride, alcohol, and certain special reagents. The experiments are best made by treating portions of the fibre or fabric in small porcelain dishes, which can afterwards be inclined so as to allow the liquid to drain to the side and permit the ready observation of any color it may have acquired. In some cases, as when fluorescence is to be looked for, it is desirable to employ test-tubes instead of porcelain capsules. Where nitric acid is employed, it should be applied to the fabric with a glass rod, when any change in the color of the spot touched will be readily seen.

I. RED COLORS.

DYESTUFF.	OBSERVER.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
			Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Magenta.	H	. .	Yellow.	Yellow.	Brown-yellow.	Yellow.	Paler.	. .
Acid Magenta.	H	B	Paler.	Pink.	Paler.	Pink.	Decolor.	. .
Safranine.	H	BSS	Blue.	Yellow.	Green.	Green.	. .	Pink.
Magdala Red.	H	. .	No change.	. .	No change.	. .	No change.	. .
Eosin A.	H	B	Yellow.	. .	Yellow.	Yellow.	Yellow.	Pink fluor.
Methyl Eosin.	H	. .	Yellow.	. .	Yellow.	Yellow.	Pink.	Pink fluor.
Phloxin.	H	. .	Yellow.	. .	Yellow.	. .	Pink.	Pink.
Erythrosin.	H	. .	Orange.	. .	Yellow.	Orange.	Pink.	Pink.
Rhodamin.	L	B	Red.	Colorless.	Red.	Colorless.	Bluer.	Colorless.
Aurin.	H	. .	Yellow.	Yellow.	Yellow.	. .	. .	Red.
Croceïn Scarlet 7 B.	H	By	Violet.	Colorless.	Blue.	Blue.	Blue.	. .
Biebrich Scarlet.	H	K	Violet.	Colorless.	Green.	Green.	Violet.	Colorless.
Patent Fast Red.	H	B	Darker.	Red.	Violet.	Colorless.	Paler.	Red.
Fast Ponceau B.	H	B	Violet.	Colorless.	Green.	Green.	Violet.	Colorless.
Scarlet 2 R.	H	M	Decolor. hot.	Extracted hot.	No action, dilute.	Extracted conc.	Decolor.	. .
Scarlet 3 R.	H	M	No change.	Red.	No action.	. .	Decolor.	Red.
Claret Red B.	H	M	No change.	Violet.	Blue.	Blue.	Orange.	Orange.
Carmoisin.	L	By	Violet.	Lilac.	Black.	Black.	Brown.	Pink.
Primuline Red.	L	BSS	Brown.	Brown.	Black.	Violet.	Brown-red.	. .
Polychromine.	. .	G	Brown.	Brown.	Black.	Violet.	Brown-red.	. .
Orseillin BB.	L	By	Black.	Blue.	Blue-black.	I lue.	Violet.	Violet.
Congo Red.	L	A	Black.	Colorless.	Black.	Blue.	No change.	. .

RED COLORS.—*Continued.*

| AMMONIA. | | SPOT WITH NITRIC ACID. | STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID. | ALCOHOL. | REMARKS. |
Fibre.	Solution.				
Decolorized.	. .	Yellow.	Decolorized.	Bluish-red.	Decolorized by sodium sulphide.
Decolor.	. .	Yellow.	Little change.	Pink.	. . .
. .	Pink.	Blue.	Decolorized.	Red, fluor.	. . .
No change.	. .	. .	Bluer.	Pink fluor.	. . .
Yellow.	Yellow fluor.	Yellow.	Yellow.	Sol. eosins not extracted; spirit eosins extracted.	. . .
Pink.	Pink fluor.	Yellow.	Decolorized.	Pink fluor.	. . .
Pink.	Pink.	Yellow.	Yellow.	Pink, with green fluorescence.	Color extracted by ammonium acetate.
Orange.	Pink.	Yellow, red rim.	Orange.	. .	. . .
Bluer.	Pink.	Yellow.	Brighter.	Fluorescent solution.	Stands boiling with soap.
. .	Red.	. .	Yellow.	Red.	. .
Blue.	. .	Dark blue.	Brown.	No action.	The spot with HNO_3 finally changes to yellow, with green rim.
No action.	No action.	Blue to brown.	Decolorized.	No action.	HNO_3 spot has a blue rim.
No action.	No action.	Blue to yellow.	Decolorized.	No action.	. . .
No action.	No action.	Blue to brown.	Decolorized.	No action.	HNO_3 spot has a black rim.
Paler.	Pink.	Violet to yellow.	Decolorized.	No action.	. . .
No change.	No change.	Violet to yellow.	Decolorized.	No action.	. . .
No change.	No change.	Violet to brown.	Decolorized.	No action.	HNO_3 spot has a blue rim.
No change.	Pink.	Violet.	Decolorized on boiling.	No action.	HNO_3 spot disappears on washing.
No change.	. .	No change.	Bright red-brown.	No action.	. . .
No change.	. .	No change.	Bright red-brown.	No action.	. . .
Violet.	Violet.	Violet.	Decolorized.	No action.	HNO_3 spot disappears on washing.
No change.	. .	Black.	Black, then decolorized.	No action.	HNO_3 spot restored to red by NH_3.

I. RED COLORS.—*Continued.*

Dyestuff.	Observer.	Firm.	Hydrochloric Acid.		Sulphuric Acid.		Caustic Soda.	
			Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Benzopur-purin B.	L	By	Brown.	Colorless.	Black.	Blue.	No change.	. .
Benzopur-purin 10 B.	L	By	Black.	Colorless.	Black.	Blue.	No change.	. .
Deltapur-purin G.	L	By	Black.	Colorless.	Black.	Blue.	No change.	. .
Deltapur-purin 5 B.	L	By	Brown.	. .	Blue.	Blue.	No change.	. .
Brilliant Congo.	L	By	Black.	Colorless.	Blue.	Blue.	No change.	. .
Rosazurin B.	L	By	Green.	Colorless.	Blue.	Blue.	No change.	. .
Congo Corinth.	L	By	Black.	. .	Black.	Blue.	Redder.	Colorless.
Hessian Purple B.	L	L	Gray.	Colorless.	Blue.	Blue.	No change.	Pink.
Hessian Purple N.	. .	L	Black.	Colorless.	Black.	Blue.	No change.	. .
Azarine S.	. .	M	Red.	Colorless.	Darker.	Red.	Bluer.	Red.
Azo-eosin.	. .	By	Dark red-violet.	Lilac.	Dark red-violet.	Lilac.	Orange.	. .
Alizarin.	. .	. .	Yellow.	Yellow.	. .	Red.	Violet.	Violet.
Alizarin S.	. .	. .	Orange.	Orange.	Orange.	Orange.	Violet.	Violet.
Alizarin Ma-roon (with chrome).	. .	B	Yellow.	Yellow.	Brown.	Brown.	Violet.	Violet.
Purpurin.	. .	B	Maroon.	Red.	Crimson.	Crimson.	Purple.	Pink.
Rose Bengal.	. .	B	Decolor.	. .	Brown.	. .	Darker.	. .
Rose Bengal B.	. .	. .	Decolor.	. .	Scarlet.	Orange.	Darker.	. .
New Magenta.	. .	M	Yellow.	Yellow.	Yellow.	Yellow.	Decolor.	. .
Scarlet R.	. .	M	Duller.	Pink.	. .	Pink.	Yellower.	. .
Brilliant Double Scar-let 3 R.	. .	By	Violet.	. .	Violet.	Violet.	Darker.	. .
Brilliant Scar-let R.	. .	C	Darker.	Pink.	Crimson.	Crimson.	Brown.	. .

I. RED COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
No change.	. .	Brown.	Decolorized.	Light red.	Picric acid turns the fibre brown.
No change.	. .	Yellow.	Decolorized.	Light red.	Picric acid turns fibre dark brown.
No change.	. .	Yellow.	Darker, then decolorized.	Light red.	Picric acid turns fibre brownish-red.
No change.	. .	Decolor-ized.	Decolorized.	Light red.	. . .
No change.	. .	Blue.	Decolorized.	Light red.	Picric acid turns fibre brown.
No change.	. .	Brown.	Decolorized.	Light red.	. . .
Redder.	Pink.	Brown.	Decolorized.	Light pink.	Fibre black with HNO_2.
No change.	Pink.	Yellow.	Decolorized.	No action.	HNO_2—violet.
No change.	. .	Brown.	Decolorized.	Bluish-red.	HNO_2—black.
Bluer.	Red.	Orange.	Yellow.	Pink.	Picric acid—brown.
Orange.	Orange.	Brown.	Decolorized on heating.	No action.	HNO_3 spot disappears on washing.
No change.	No change.	Yellow.	Yellow.	No action.	$Ba(OH)_2$—violet. Gives no fluores. sol. with $Al_2(SO_4)_3$ on boiling (distinction from madder and purpurin).
Violet.	Colorless.	Yellow.	Orange, turned violet by NaOH.	No action.	Ash contains Al or Cr.
No change.	No change.	Brown.	Red on heating.	No action.	Ash contains Cr.
No change.	Pink.	Yellow.	Red, liquid yellow.	Red.	$Ba(OH)_2$—red. Fluores. sol. with boiling solution of $Al_2(SO_4)_3$.
No change.	Pink.	Yellow.	Decolorized.	Pink.	. . .
Darker.	Pink.	Yellow.	Decolorized.	Bluish-pink.	. . .
Decolor.	. .	Yellow.	Decolorized.	Bluish-red.	. . .
Brighter.	. .	Yellow.	Decolorized.	No action.	. . .
Pink.	. .	Yellow.	Decolorized.	. .	. . .
No change.	Pink.	Yellow.	Decolorized.	. .	. . .

I. RED COLORS.—*Continued.*

Dyestuff.	Firm.	Hydrochloric Acid.		Sulphuric Acid.		Caustic Soda.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Brilliant Scarlet.	C	No change.	. .	Purple.	Purple.	Brown.	Brown.
Bordeaux extra.	By	Violet.	. .	Violet.	Violet.	Maroon.	Brown.
Bordeaux G.	By	Violet.	Blue.	Blue.	Blue.	Purple.	. .
Brilliant Croceine.	C	Purple.	Blue.	Violet.	Violet.	Purple.	. .
Azo-Carmine.	B	Darker.	Red.	Green.	Green.	Maroon.	. .
Azo-Fuchsine G.	By	Brighter.	Pink.	Violet.	Black.	Violet.	Violet.
Azo-Fuchsine B.	By	No change.	Pink.	Crimson.	Red.	Red.	. .
Alizarin GG (Cr mordant).	B	Brown.	Yellow.	Crimson.	Crimson.	Maroon.	. .
Alizarin V (Cr mordant).	B	Brown.	Yellow.	Crimson.	Crimson.	Darker.	. .
Alizarin Bordeaux B (Cr mordant).	By	Maroon.	Brown.	Violet.	Violet.	Violet.	Blue.
Brilliant Congo R.	By	Brown.	Colorless.	Blue.	Blue.	Yellower.	. .
Benzo-Purpurin 4 B.	By	Blue.	Colorless.	Blue.	Blue.	No change.	. .
Brilliant Purpurin R.	. .	Blue.	Colorless.	Blue.	Blue.	No change.	. .
Crystal Scarlet.	C	Crimson.	. .	Violet.	Violet.	Brown.	. .
Croceine Scarlet 3 B.	By	Blue.	Blue.	Blue.	Blue.	Purple.	. .
Croceine 3 BX.	By	Crimson.	Pink.	Purple.	Purple.	Brown.	. .
Cochineal Red A.	B	Darker.	. .	Crimson.	. .	Brown.	Brown.
Cochineal Red 3 R.	B	Purple.	Purple.	Purple.	Purple.	Brown.	Brown.
Cyanosin.	M	Orange.	. .	Orange.	. .	No change.	. .
Cyclamin.	Mo	Flesh.	. .	Brown.	Brown.	. .	. .
Cloth Red G.	O	Violet.	Blue.	Violet.	Blue.	Darker.	. .
Cloth Red B.	By	Violet.	. .	Blue.	Black.	Crimson.	. .
Cloth Red 3 G.	By	Violet.	. .	Blue.	Black.	Darker.	. .
Clayton Cloth Red.	Cl	Crimson.	. .	Purple.	Violet.	Crimson.	. .

I. RED COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Darker.	Pink.	. .	. .	. .	. . .
Crimson.	Pink.	Yellow; blue rim.	Bluer.	Light pink.	. . .
Darker.	. .	. .	. .	Pink.	. . .
Bluer.	. .	Blue.	Decolorized.	. .	. . .
Bluer.	Pink.	.	. .	Crimson.	. . .
Scarlet.	Red.	Orange.	Decolorized.	Light red.	. . .
Red.	Orange.	Red.	Decolorized.	Light red.	. . .
Maroon.	Colorless.	Orange.	Darker.	No action.	. . .
Darker.	Colorless.	Orange.	Brown.	No action.	. . .
Violet.	. .	Red.	. .	No action.	. . .
No change.	. .	Red.	Decolorized.	Light red.	. . .
No change.	. .	Yellow.	Decolorized.	Light red.	. . .
No change.	. .	Yellow.	Decolorized.	Light pink.	. . .
. .	Pink.	Yellow.	. .	Light pink.	. . .
. .	Pink.	Yellow; blue rim.	Decolorized.	. .	. . .
Browner.	. .	Yellow.	Decolorized on boiling.	. .	. . .
. .	Pink.	Yellow.	. .	. .	. . .
. .	Pink.	Yellow; violet rim.	Lighter.	. .	. . .
No change.	. .	Yellow.	Orange.	Pink fluor.	. . .
. .	Pink.	Yellow.	Decolorized.	. .	. . .
Darker.	. .	Red.	. .	Scarlet.	. . .
Crimson.	Pink.	Yellow.	Bluer.	Crimson.	. . .
Brighter.	. .	Yellow; purple rim.	. .	Light red.	. . .
Brighter.	Pink.	. .	Darker.	Light red.	. . .

I. RED COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Congo Corinth G.	. .	Blue.	Colorless.	Blue.	Blue.	Redder.	Colorless.
Congo Corinth B.	.	Purple.	Colorless.	Blue.	Blue.	Redder.	Colorless.
Croceine Scarlet 3 B.	. .	Blue.	Blue.	Blue.	Blue.	Decolorized.	Gray.
Congo Red 4 R.	. .	Blue.	Colorless.	Blue.	Blue.	No change.	. .
Diamine Fast Red.	C	Violet.	Colorless.	Purple.	Blue.	Brown.	Colorless.
Diamine Scarlet B.	C	Violet.	Violet.	Violet.	Violet.	Orange.	Colorless.
Diamine Red NO.	C	Olive.	Colorless.	Blue.	Blue.	No change.	. .
Diamine Red 3 B.	C	Yellow.	Colorless.	Blue.	Blue.	No change.	. .
Erika B.	A	Redder.	Colorless.	Purple.	Violet.	Bluer.	Colorless.
Fast Red A.	B	Purple.	. .	Violet.	Violet.	Maroon.	. .
Fast Red B.	B	Crimson.	Pink.	Violet.	Purple.	Red.	. .
Fast Red C.	B	Darker.	Pink.	Violet.	Violet.	. .	. .
Fast Red D.	B	Darker.	Pink.	Violet.	Violet.	Brown.	. .
Fast Red E.	B	Maroon.	Pink.	Purple.	Purple.	Brown.	. .
Fast Red BT.	By	Darker.	. .	Violet.	Violet.	Red.	. .
Fluoresceïne.	B	Yellow.	Yellow.	Yellow.	Yellow.	. .	Yellow; green fluor.
Geranine.	. .	No change.	. .	Crimson.	Pink.	Violet.	Colorless.
Phloxine 2 B.	. .	Red.	. .	Brown.	. .	Darker.	. .
Scarlet 6 R.	M	Crimson.	Pink.	Violet.	Violet.	Brown.	. .
Scarlet GG.	M	. .	Pink.	Darker.	Scarlet.	Orange.	. .
Scarlet S extra.	A	Brown.	Blue.	Bluer.	Blue.	Violet.	. .
Milling Red R.	C	Maroon.	. .	Purple.	Purple.	Redder.	. .
Orchil Red.	B	Violet.	. .	Blue.	Blue.	Maroon.	. .
Scarlet 2 S.	A	Yellow.	Pink.	Orange.	Pink.	Orange.	. .
Palatine Scarlet.	B	Darker.	Pink.	Crimson.	Magenta.	Brown.	. .
Palatine Red.	B	Bluer.	. .	Blue.	Blue.	Brown.	Brown.
Roxamine.	D	Bluer.	. .	Violet.	Violet.	Purple.	. .
Safrosine.	Lev	Decolor.	. .	Yellow.	Yellow.	Darker.	. .

1. RED COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Brighter.	Pink.	Brown.	Decolorized.	Light red.	. . .
Redder.	Pink.	Brown.	Decolorized.	Purple.	. . .
Lighter.	Scarlet.	Blue to yellow.	Decolorized.	Scarlet.	. . .
No change.	Pink.	Orange.	Decolorized.	Light orange.	. . .
No change.	. .	Brown.	Decolorized.	Light pink.	. . .
Orange,	. .	Crimson.	Decolorized.	Pink.	. . .
No change.	Pink.	Brown.	Decolorized.	Light red.	. . .
No change.	Pink.	Brown.	Decolorized.	Orange-red.	. . .
No change.	Pink.	Red.	Decolorized.	Light pink.	. .
Darker.	. .	Yellow.	Lighter.	Pink.	. . .
. .	. .	Yellow.	Lighter.	Pink.	. .
Brighter.	Pink.	Yellow.	Lighter.	Pink.	. . .
Darker.	Brown.	Yellow.	Lighter.	Pink.	. . .
Darker.	Red.	Yellow.	Brighter.	Pink.	. . .
Darker.	. .	Yellow.	Lighter.	Red.	. . .
. .	Yellow, green fluor.	. .	Yellow.	Green fluores.	. . .
Violet.	Violet.	No change.	Decolorized.	Pink.	. . .
Darker.	Pink.	Yellow.	Decolorized.	. .	. . .
.	Pink.	Yellow.	. .	. .	. . .
. .	Pink.	. .	. .	. .	. . .
Bluer.	Pink.	Yellow.	Crimson.	. .	. . .
No change.	. .	Orange.	. .	. .	. . .
Crimson.	. .	Orange.	. .	Pink.	. . .
Yellower.	. .	Yellow.	. .	. .	. . .
Lighter.	. .	Yellow.	. .	. .	. . .
Redder.	. .	. .	Decolorized.	. .	. . . .
Purple.		Yellow.	.	Light red.	HNO_3—blue rim.
Darker.	Pink.	Yellow.	Decolorized.	Pink.	. . .

I. RED COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Orchil Sub-stitute V.	P	Crimson.	Crimson.	Crimson.	Crimson.	Maroon.	. .
Orchil Sub-stitute 3 VN.	P	Crimson.	Crimson.	Crimson.	Crimson.	Maroon.	. .
Fast Violet B. (Violamin B.)	M	Violet.	. .	Scarlet.	Red.	Violet.	.
Fast Violet R. (Violamin R.)	M	Bluer.	Pink.	Red.	Red.	Red.	. .
Orchil Red G.	A	Crimson.	Pink.	Purple.	Purple.	Darker.	. .
Naphthylene Red.	. .	Green.	Colorless.	Blue.	Blue.	No change.	. .
St. Denis Red.	P	Bluer.	Colorless.	Crimson.	Crimson.	Orange.	Orange.
Poppy 2 R. Xylindine Red.	M	. .	Red.	Darker.	Red.	Decolor-ized.	Red.
Poppy 3 R. Cumidine Red.	M	Red.	Red.	Darker.	Red.	Brown.	Brown.
Wool Scarlet R.	Sch	Darker.	Rose.	Darker.	Red.	Orange.	Red.
Pyrotin R PO.	D	Violet.	Colorless.	Violet.	Violet	Brown.	Brown.
Ponceau 6 R.	M	. .	Violet.	Violet.	Magenta.	Brown.	Brown.
Toluylene Red. Neutral Red.	C	Blue.	Blue.	Green.	Green.	Olive.	.
Pyronine B.	L	Orange.	Orange.	Orange.	Orange.	Orange.	Colorless.
Stilbene Red.	A	Black.	Colorless.	Violet.	Colorless.	. .	Pink.
Alkali Red.	D	Blue.	Colorless.	Blue.	Blue.	. .	Pink.
Chromotrop 2 R.	M	No change.	Pink.	Dark red.	Dark red.	Redder.	Pink.
Titan Scarlet.	H	Dark red.	Dark red.	Magenta.	Magenta.	Dark red.	Red.
Atlas Red.	BSS	No action.	Colorless.	Crimson.	Crimson.	No action.	. .
Dianthine.	BSS	Darker.	. .	Crimson.	Crimson.	Orange.	. .
Ingrain Ma-roon.	BSS	No change.	. .	Maroon.	Maroon.	No change.	. .
Acid Milling Scarlet.	BSS	Brownish.	Colorless.	Maroon.	Maroon.	Darker.	. .
Rock Scarlet SY.	BSS	Brownish.	Colorless.	Maroon.	Maroon.	No change.	. .

I RED COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Maroon.	. .	Yellow.	Lighter.	. .	. . .
Maroon.	. .	Yellow.	Lighter.	Pink.	. . .
Redder.	Pink.	Scarlet.	. .	Violet.	. . .
. .	Pink.	Scarlet.	. .	. .	. . .
Bright.	Red.	Yellow.	. .	Light red.	. . .
No change.	. .	Green.	Decolorized.	Light pink.	. . .
Orange.	Orange.	No change.	Decolorized.	Red.	. . .
Brighter.	.	Yellow.	Decolorized.	No action.	. . .
No change.	No change.	Yellow.	Decolorized.	Light pink.	. . .
Orange.	Red.	Darker.	. .	. .	. . .
. .	Orange.	Blue.	Decolorized.	. .	Color extracted with hot $NH_4C_2H_3O_2$ solution.
. .	Violet	Scarlet.	Decolorized.	. .	Color extracted with hot $NH_4C_2H_3O_2$ solution.
Orange.	Orange.	Blue.	Decolorized.	Red.	Color extracted by hot $NH_4C_2H_3O_2$ solution.
Brighter.	Yellow.	Scarlet.	Decolorized.	Red; green fluor.	Color extracted by hot $NH_4C_2H_3O_2$ solution,
. .	Pink.	Violet.	Decolorized.	No action.	. . .
. .	Orange.	Olive.	Decolorized.	No action.	. . .
Lighter.	Pink.	Yellow.	Decolorized.	No action.	Boiled with alum—violet.
. .	Orange.	Orange.	Decolorized.	Scarlet.	. .
No change.	Brown.	Brown.	Yellow.	Light brown.	On reduction it gives primuline.
Paler.	Orange.	Darker.	Decolorized.	Light pink.	. . .
. .	Pink.	Maroon.	Yellow.	No action.	On reduction it gives primuline.
Paler.	Orange.	Yellow.	Pink.	Light pink.	. . .
No change.	. .	Yellow.	Decolorized.	Light pink.	Resists boiling soap solution.

I. RED COLORS.—*Concluded.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Rock Scarlet BS.	BSS	Browner.	Colorless.	Maroon.	Maroon.	No change.	. .
Clayton Cloth Scarlet.	Cl	Darker.	Magenta.	Magenta.	Ruby.	Maroon.	Reddish.
Cochineal Scarlet G.	Sch	Brownish.	. .	Bluer.	. .	Orange	Orange.
Cochineal Scarlet R.	Sch	Brownish.	. .	Purple.	Colorless.	Orange.	Orange.
Cochineal Scarlet 2 R.	Sch	Brownish.	. .	Purple.	Colorless.	Orange.	Orange.
Wool Scarlet G.	Sch	No change.	. .	No change.	. .	Orange.	Orange.
Wool Scarlet R.	Sch	No change.	. .	No change.	. .	Orange.	Orange.
Wool Scarlet 2 R.	Sch	No change.	. .	No change.	. .	Orange.	Orange.
Buffalo Rubine.	Sch	Violet.	. .	Blue.	Violet.	Ruby.	Ruby.
Cotton Scarlet 3 B.	Sch	Violet.	. .	Violet..	Colorless.	Violet.	Violet.
Brilliant Red.	Sch	Violet.	. .	Violet.	Colorless.	Brownish.	Brown.
Madder.	. .	Brown-red.	. .	Brown-red.	Red.	Purple.	Purple.
Orchil.	. .	No change.	Red.	Purple.	Purple.	Purple.	. .
Brazil wood.	. .	Dark red.	Pink.	Brown.	Yellow.	Maroon.	Violet.
Barwood.	. .	Redder.	. .	Red-brown.	Dirty brown.	Purple.	Colorless.
Sanderswood.	. .	Browner.	. .	Red-brown.	Red-brown.	Purple.	Colorless.
Safflower.	. .	Decolor-ized.	. .	Decolor-ized.	. .	Pale yellow.	. .
Cochineal.	. .	Orange.	Orange.	Pink.	Pink.	. .	Purple.
Ammoniacal Cochineal.	. .	Orange.	Orange.	Yellow-brown.	. .	Bluer.	. .

I. RED COLORS.—*Concluded.*

Ammonia.		Spot with Nitric Acid.	Stannous Chloride and Hydrochloric Acid.	Alcohol.	Remarks.
Fibre.	Solution.				
No change.	Pink.	Yellow.	Decolorized.	No action.	Resists boiling soap solution.
. .	Pink.	Yellow.	Decolorized.	No action.	. . .
Yellower.	Orange.	Yellow.	Decolorized.	Scarlet.	. . .
Yellow.	Orange.	Yellow.	Decolorized.	Scarlet.	. . .
Yellow.	Yellow.	Yellow.	Decolorized.	Scarlet.	. . .
Yellower.	Yellow.	Yellow.	Decolorized.	No action.	. . .
Yellower.	Yellow.	Yellow.	Decolorized.	No action.	. . .
Yellower.	Yellow.	Yellow.	Decolorized.	No action.	. . .
Dull red.	Red.	Yellow.	Decolorized.	No action.	. . .
Violet.	. .	Orange.	Decolorized.	No action.	. . .
No change.	. .	Orange.	Decolorized.	Red.	. . .
Brown-red.	. .	Yellow.	Terra-cotta.	No action.	. . .
Purple.	. .	. .	Decolorized.	Purple.	Ash contains Al.
Violet.	Violet.	Yellow.	Violet.	Pale yellow.	. . .
Purple.	Colorless.	Olive.	No change.	Red.	. . .
Purple.	Colorless.	Olive.	No change.	Red.	$FeSO_4$—violet.
Pink.	. .	. .	Yellow.	No action	On cotton fibre.
. .	Purple.	Yellow.	Orange.	No action.	Sn mordant.
Violet.	. .	. .	. .	. .	Ash contains Al.

II. VIOLET COLORS.

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Gallein.	B	Brown-red.	Amber-yellow.	Like HCl.	Like HCl.	Paler.	. .
Fast Violet.	By	Dark blue.	Blue.	Black.	Blue.	Black.	Violet.
Azo-Violet.	. .	Black.	Colorless.	Black.	Green.	Crimson.	Colorless.
Hessian Violet.	. .	Dark blue.	Colorless.	Dark blue.	Black.	Redder.	Colorless.
Heliotrope.	. .	Black.	Blue.	Blue-black.	Blue.	Crimson.	Colorless.
Methyl Violet.	. .	Brown.	Amber.	Brown.	Amber.	Decolor.	. .
Phenyl Violet or Spirit Violet.	. .	Dark green.	Brown.	Brown.	Brown.	Decolor.	. .
Benzyl Violet.	.	Brown.	Amber.	Brown.	Amber.	Decolor.	. .
Acid Violet 7 B.	By	Green.	Amber.	Blackish.	Red.	Decolor.	Colorless.
Perkin's Violet.	. .	No change.	Pink.	No change.	. .	Blue.	.
Gallocyanin.	DH	Violet.	Violet.	Black.	Blue.	Black.	Violet.
Muscarin.	DH	Black.	Blue.	Black.	Green.	Black.	Colorless.
Alizarin.	. .	Yellow.	Yellow.	Yellow.	Yellow.	Bluer.	. .
Acid Violet BB.	B	Yellow.	. .	Yellow.	Yellow.	Decolor.	. .
Acid Violet 6 B.	By	Orange.	Yellow.	Orange.	Yellow.	Decolor.	. .
Acid Violet 4 BN.	B	Yellow.	Yellow.	Yellow.	. .	Decolor.	. .
Acid Violet 4 RS.	B	Decolorized.	. .	Yellow.	Yellow.	Decolor.	. .
Alkali Violet.	B	Orange.	Yellow.	Orange.	Yellow.	Decolor.	. .
Azarin.	M	. .	. .	Crimson.	Crimson.	. .	. .
Azo-Mauve N.	. .	Blue.	. .	Blue.	. .	Redder.	. .
Fast Acid Violet 10 B.	By	Green.	. .	Green.	. .	. .	. .
Formyl Violet 4 BS.	C	Yellow.	Yellow.	Yellow.	Yellow.	Decolor.	. .
Chrome Violet.	By	Crimson.	Pink.	Yellow.	Yellow.	Lighter.	. .
Crystal Violet 6 B.	B	Orange.	Yellow.	Orange.	Yellow.	Lighter.	Colorless.
Methyl Violet 6 B.	A	Orange.	Yellow.	Orange.	Yellow.	Lighter.	Colorless.
Ethyl Purple.	B	Orange.	Yellow.	Orange.	Yellow.	Bluer.	. .
Regina Violet.	A	Gray.	Brown.	Brown.	Brown.	Decolor.	. .

II. VIOLET COLORS.

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Paler.	. .	Yellow.	Crimson.	No action.	Ash contains Cr.
No change.	Violet.	Black.	Decolorized.	Violet.	. . .
Violet.	Magenta.	Red.	Decolorized.	No action.	Picric acid—black.
Redder.	Violet.	Blue rim.	Blue then de-colorized.	No action.	. . .
No change.	. .	. .	Decolorized.	No action.	Picric acid—dark brown.
Lilac.	. .	. .	Green.	Violet.	. . .
Decolor-ized.	. .	Green.	Decolorized slowly.	Violet.	. . .
Lavender.	. .	. .	Green.	Violet.	. . .
Decolor.	Colorless.	Olive.	Green.	Light violet.	. . .
No change.	. .	No change.	Brown.	Violet.	. . .
Black.	Violet.	. .	Gray.	No action.	. . .
Blue.	Violet.	Black.	Gray.	No action.	. . .
No change.	. .	. .	Yellow.	No action.	. . .
Decolor.	. .	Yellow.	Bluer.	Light violet.	. . .
Lighter.	. .	Yellow.	Green.	Light violet.	. . .
Decolor.	. .	Yellow.	Green.	Violet.	. . .
Decolor.	. .	Yellow.	No change.	Red-violet.	. . .
Decolor.	. .	Yellow.	Green.	No action.	. . .
. .	. .	Brown.	Brighter.	Purple.	. . .
Redder.	. .	. .	Decolorized.	Violet.	. . .
. .	Blue.	Green.	. .	Blue.	. . .
Lighter.	. .	Yellow.	Green.	Light violet.	. . .
Lighter.	. .	Yellow; red rim.	. .	Light violet.	. . .
Lighter.	Colorless.	Yellow.	Green.	Violet.	. . .
Lighter.	Colorless.	Yellow.	Blue.	Violet.	. . .
Bluer.	. .	Yellow.	Green.	Violet.	. . .
Decolor.	. .	Yellow.	Bluer.	Violet.	. . .

II. VIOLET COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Heliotrope 2 B.	. .	Bluer.	Colorless.	Violet.	Violet.	Crimson.	Pink.
Diamine Violet N.	C	Blue.	Colorless.	Blue.	Blue.	Redder.	Colorless.
Congo Violet.	A	Bluer.	. .	Bluer.	Violet.	Red.	Colorless.
Naphthyl Violet.	K	Redder.	. .	Green.	. .	Gray.	. .
Congo Corinth B.	By	Blue.	Colorless.	Blue.	Colorless.	Red.	Colorless.
Red Violet 4 RS.	B	Redder.	Violet.	Dark red.	. .	Decolor-ized.	Colorless.
Fast Bluish Violet.	By	Blue.	Colorless.	Green.	Green.	Bluer.	Violet.
Victoria Violet.	M	Redder.	Rose.	Bluer.	Violet.	Red.	Colorless.
Hofmann's Violets.	BSS	Yellow.	Colorless.	Yellow.	. .	Decolor-ized.	. .
Regina Purple.	BSS	Brown.	Colorless.	Brown.	Colorless.	Decolor.	. .

III. BLUE COLORS.

Resorcin Blue.	. .	. .	. .	No change.	. .	. .	Blue, red fluor.
Benzo Azurin G.	By	Black.	Colorless.	Black.	Blue.	Dark red.	Pink.
Azo Blue.	By	Black.	Colorless.	Black.	Blue.	Red.	Pink.
Soluble Blue.	BSS	. .	Blue.	Red brown.	Red brown.	Red brown.	. .
Spirit Blue.	P	Green.	Brown.	Red brown.	Red brown.	Brick red.	. .
Alkali Blue 3 B.	B	Blue.	Colorless.	Red brown.	Red brown.	Decolor-ized.	. .
Victoria Blue.	B	Black.	Red.	Black.	Orange.	Brown.	Colorless.
Indulines.	. .	Violet.	Blue.	. .	Dark blue.	. .	Violet de-color. by Zn dust.
Basle Blue.	DH	Gray.	Yellow.	Yellow.	Yellow.	Darker.	. .
Indophenol Blue.	. .	Brown.	. .	Brown.	. .	No change.	. .
Vat Indigo Blue.	. .	No change.	. .	. .	Blue.	No change.	. .
Indigo Car-mine.	. .	No change.	Bluish.	. .	Violet.	Greenish.	Brown.

Il. VIOLET COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO- CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
No change.	. .	Orange.	Decolorized.	No action.	. . .
Redder.	Colorless.	Brown.	Decolorized.	No action.	. . .
Paler.	Red.	Brown.	Decolorized.	No action.	. . .
No change.	. .	Red.	Redder.	No action.	. . .
Red.	Rose.	Blue.	Decolorized.	Rose.	. . .
Decolor- ized.	Colorless.	Dark red.	No change.	No action.	. . .
Paler.	Violet.	Scarlet.	Decolorized.	No action.	. . .
Red.	Colorless.	Orange.	Decolorized.	No action.	. . .
Paler.	. .	Yellow.	Yellow.	Violet.	. . .
Decolor.	Colorless.	Yellow.	Brown.	Violet.	. . .

III. BLUE COLORS.

	Blue, red fluor.	.	. .	. .	. . .
Dark violet.	Red.	. .	Decolorized slowly.	No action.	Boiling soap solu- tion—blue.
Dark violet.	Red.	. .	Decolorized.	No action.	Picric acid—brown.
Decolor- ized.	. .	Green.	Color extract.	No action.	. . .
Decolor- ized.	. .	. .	No change.	Blue.	HNO_2—black spot.
Decolor- ized.	. .	. .	No change.	Blue.	HNO_2—light green.
Green.	Colorless.	Brown.	Dark blue.	Blue.	. . .
. .	As NaOH.	Dark green.	Violet solu- tion.	Blue-violet.	Induline NN not changed by CaO- Cl_2.
No change.	. .	Black.	No change.	Light blue.	. . .
No change.	. .	. .	Decolorized.	Blue.	Boiled with olive oil —color extracted.
No change.	. .	Yellow.	Paler; solu- tion yellow.	Blue.	Chloroform ex- tracts color.
As NaOH.	As NaOH.	Yellow.	Decolorized.	No action.	Boiling dil. Na_2CO_3 —color extracted.

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III. BLUE COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Logwood Blue.	. .	Red.	Red.	As HCl.	As HCl.	Purple.	Purple.
Prussian Blue.	. .	No action.	. .	No action.	. .	Brown.	. .
Ultramarine Blue.	. .	Decolor-ized.	. .	Decolor-ized.	. .	No action.	. .
New Blue.	C	Purple.	. .	Gray.	Gray.	Violet.	Pink.
Naphthalene Blue G.	By	Violet.	Orange.	Black.	Brown.	Brown.	Orange.
Nile Blue.	B	Yellow.	Yellow.	Red.	Red.	Red.	Pink.
Alizarin Blue.	B	Violet.	Orange.	Violet with di-lution.	Red with dilution.	Greenish.	. .
Methylene Blue.	B	Decolor-ized.	Blue-green.	Green.	Green.	Violet.	.
Alizarin Cyanin R.	By	Redder.	Blue.	Violet.	Violet.	Greener.	. .
Alizarin Indigo Blue.	B	Darker.	Pink.	Darker.	Violet.	Greener.	Colorless.
Toluidine Blue.	M	No change.	Blue.	Olive.	Greenish.	Crimson.	. .
Thiocarmin R.	C	Green.	Green.	Green.	Green.	Darker.	. .
Alkali Blue 4 B.	C	Redder.	Light green.	Red.	Red.	Brown.	. .
Cyanin B.	M	Yellow.	. .	Yellow.	. .	Olive.	. .
Chrome Blue.	By	Crimson.	Pink.	Crimson.	Maroon.	. .	. .
Patent Blue.	M	Amber.	Yellow.	Yellow.	. .	Green.	Blue.
Pure Soluble Blue.	C	Brighter.	Light blue.	Red.	Red.	Red.	. .
Neutral Blue.	C	Orange.	Yellow.	Orange.	Yellow.	Lighter.	. .
Victoria Blue B.	B	Red.	Red.	Red.	Red.	Maroon.	Colorless.
Indazine.	C	Darker.	Blue.	Dark green.	. .	Redder.	. .
Metaphenyl-ene Blue.	C	. .	Blue.	Gray.	. .	Duller.	. .
Indamine Blue B.	M	Darker.	Blue.	Darker.	Blue.	Purple.	. .
Indoin Blue.	B	Green.	Slate.	Olive.	Olive.	Violet.	Pink.
Paraphenyl-ene Blue.	D	Darker.	Blue.	Darker.	Blue.	Purple.	. .

III. BLUE COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Purple.	Purple.	. .	Brown.	No action.	. . .
No action.	. .	Green.	No action.	No action.	Ash contains Fe.
No action.	. .	. .	Decolorized.	No action.	Blue ash.
Violet.	Pink.	. .	Green, then decolorized.	Light blue.	. . .
Violet.	Brown.	. .	Decolorized.	Light violet.	HCl gas—brown.
Violet.	. .	Green, yellow rim.	Decolorized.	Pale blue.	. . .
No action.	. .	Yellow, turning brown.	Violet, red on heating.	No action.	Ash contains Cr.
No action.	. .	Green.	Decolorized.	Greenish-blue.	$CaOCl_2$—decolorized.
. .	. .	Green.	Redder.	Light violet.	. . .
Greener.	. .	Yellow, violet rim.	. .	. .	. . .
. .	. .	Olive.	Decolorized.	Blue.	. . .
Darker.	. .	Green.	Greener.	Bluish-green.	. . .
Decolorized.	Blue.	Green.	. .	Blue.	. . .
Bright.	Pale blue.	Yellow.	. .	Green-blue.	. . .
. .	. .	Yellow.	Greener.	Blue.	. . .
No change.	Colorless.	Yellow.	Yellow.	No action	. . .
Decolorized.	. .	Green.	No change.	Blue.	. . .
Lavender.	. .	Green.	Green.	Violet.	. . .
Violet.	Colorless.	Green.	Darker.	Blue.	. . .
. .	. .	Maroon.	. .	Violet.	. . .
. .	. .	Green.	. .	. .	. . .
. .	. .	Green.	. .	Blue.	. . .
. .	. .	Green.	Greener.	Blue.	. . .
Violet.	. .	Yellow.	Lighter.	. .	. . .

III. BLUE COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Benzo Black Blue.	By	Greener.	Colorless.	Green.	Blue.	Darker.	Colorless.
Night Blue.	B	Red.	Red.	Red.	Red.	Brown.	.
Naphthylene Blue R.	. .	Dark blue.	. .	Dark blue.	. .	Brown.	. .
Diamine Blue BX.	C	Violet.	Colorless.	Green blue.	Blue.	Violet.	Colorless.
Diamine Blue 3 R.	C	Darker.	Colorless.	Green blue.	Blue.	Magenta.	Pink.
Benzo Azurin.	. .	No change.	. .	Green blue.	Blue.	Crimson.	Pink.
Brilliant Azurin 5 G.	. .	No change.	. .	Blue green.	Light green.	Violet.	Colorless.
Benzo Azurin 3 G.	. .	Darker.	Colorless.	Green blue.	Blue.	Violet.	Pink.
Diamine Blue 6 G.	C	No change.	. .	Olive gray.	.	Redder.	Colorless.
Benzo Black Blue G.	. .	No change.	. .	Green.	. .	No change.	. .
Sulphon Azurin.	. .	Violet.	Colorless.	Violet.	Violet.	No change.	. .
Bavarian Blue DSF.	A	. .	Bluish.	Red.	Red.	Red.	Colorless.
Wool Blue S.	B	Yellow.	Colorless.	Orange.	Orange.	Decolor.	. .
Naphthyl Blue.	K	Redder.	. .	Green.	. .	Green blue.	Colorless.
Capri Blue NO.	L	Violet.	Violet.	Dark green.	Green.	Green.	Colorless.
Gallamine Blue.	G	. .	Violet.	. .	Violet.	Darker.	. .
Azophenine Blue R and G.	N	. .	Blue.	.	Dark blue.	Violet.	. .
Heligoland Blue 3 B.	N	Redder.	. .	Green blue.	Violet.	Violet.	. .
Keton Blue B.	M	Yellow.	. .	Yellow.	. .	Green.	. .
Diamine Sky Blue FF.	C	Darker.	. .	Green.	Green.	Redder.	Violet.
Diamine New Blue G.	C	Violet.	. .	Green.	. .	Darker.	. .
Diamine Brilliant Blue G.	C	Darker.	. .	Green.	. .	Violet.	Violet.
Brilliant Azurine B.	By	No change.	. .	Green.	. .	. .	Magenta.

III. BLUE COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
No change.	. .	Red.	Decolorized.	No action.	. . .
Gray.	. .	Red.	Greener.	Blue.	. . .
Brown.	. .	. .	Decolorized.	Blue.	. . .
Violet.	Colorless.	Brown.	Decolorized.	Pale violet.	On cotton.
Violet.	Pink.	Yellow.	Decolorized.	Violet.	On cotton.
Violet.	Pink.	Brown.	Decolorized.	Violet.	On cotton.
Violet.	Colorless.	Crimson.	Decolorized.	Pale blue.	On cotton.
Violet.	Pink.	Orange.	Decolorized.	Violet.	On cotton.
No change.	. .	Yellow.	Violet.	Pale blue.	On cotton.
No change.	. . .	Red.	Decolorized.	Pale blue.	On cotton.
No change.	. .	Yellow.	Decolorized.	Blue.	On cotton.
Decolor-ized.	Colorless.	Green.	Decolorized.	No action.	. . .
Decolor.	. .	Yellow.	Decolorized.	No action.	. . .
Green blue.	Colorless.	Violet.	No action.	No action.	. . .
No action.	. .	Green.	Decolorized.	Pale blue.	. . .
. .	Violet.	Orange.	Yellow.	No action.	. . .
Redder.	. .	Violet.	Lighter.	. .	. . .
Violet.	. .	Orange.	Decolorized.	. .	On cotton.
No change.	. .	Yellow.	Green.	. .	. . .
Darker.	Blue.	Red violet.	Decolorized.	. .	On cotton.
No change.	. .	Violet,	Decolorized.	. .	On cotton.
. .	Violet.	Violet.	Decolorized.	. .	On cotton.
. .	Violet.	Red.	Decolorized.	. .	On cotton.

III. BLUE COLORS.—*Concluded.*

Dyestuff.	Firm.	Hydrochloric Acid.		Sulphuric Acid.		Caustic Soda.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Acid Alizarin Blue BB.	M	No change.	. .	Violet.	. .	Bluer.	. .
Diaminogene Extra.	C	No change.	. .	Dull blue.	. .	No change.	. .
Alizadine Blue.	H	. .	Blue.	Blue.	Blue.	Violet.	. .
Diamine Dark Blue B.	C	Darker.	. .	Violet.	. .	. .	Violet.
Diaminogene Blue G.	C	Greener.	. .	. .	Violet.	Redder.	. .
Keton Blue 4 BN.	M	Yellow.	. .	Yellow.	. .	Olive.	. .
Diamine Azo Blue R.	C	No change.	. .	. .	Blue.	Violet.	Red.
Brilliant Alizarin Cyanine 3 G.	By	Drab.	. .	Brown.	. .	Greener.	Blue.
Titan Ingrain Blue.	H	No change.	Pale green.	Green blue.	. .	Violet.	Pink.
Titan Como SN.	H	No change.	. .	Red.	. .	Violet.	. .
Anthracene Blue SWX.	B	. .	Violet.	. .	Blue.	Deeper.	. .
Coomassie Navy Blue R.	Lev	No change.	. .	Green.	. .	Violet.	. .
Paramine Navy Blue 2 R.	. .	Redder.	. .	. .	Blue.	. .	Violet.
Paramine Blue B.	. .	Redder.	. .	. .	Indigo blue.	. .	Violet.
Lanacyl Blue BB.	C	Maroon.	. .	. .	Green.	Red.	. .
Lanacyl Navy Blue B.	C	No change.	. .	. .	Bluish green.	. .	Violet.

III. BLUE COLORS.—*Concluded.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDROCHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Bluer.	. .	Violet.	. .	. .	. . .
. .	. .	Brown.	Violet.	. .	On cotton, diaz. and developed.
. .	. .	Violet.	Dark green.	. .	. . .
. .	. .	Crimson.	Decolorized.	. .	. . .
. .	. .	Red.	Decolorized.	. .	Diaz. and developed with beta-naphthol.
. .	. .	Yellow.	Green.	. .	. . .
. .	. .	Crimson.	Violet.	. .	Diaz. and developed.
. .	. .	Drab.	Yellow.	. .	. . .
. .	. .	Crimson.	Gray.	. .	Diaz. and developed.
. .	. .	Green.	No change.	. .	. . .
.	. .	Brown.	Violet.	. .	. . .
. .	. .	Crimson.	Decolorized.	. .	. . .
. .	. .	Crimson.	Decolorized.	. .	. . .
. .	. .	Crimson.	Decolorized.	. .	. . .
. .	. .	Crimson.	Decolorized.	. .	. . .
. .	. .	Crimson.	Pale green.	. .	. . .

IV. GREEN COLORS.

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Cœruleïn.	B	Duller.	Claret.	Duller.	Amber.	No action.	. .
Resorcin Green.	DH	Yellow.	Red.	Brown.	Brown.	Darker.	Greenish.
Acid Green.	. .	Pale green.	. .	Brown.	Yellow.	Decolor.	. .
Alkali Green.	.	Olive.	Brown.	Dk. brown.	Dk. brown.	Decolor.	. .
Methyl Green.	B	Yellow.	Yellow.	Bleached.	Colorless.	Decolorized.	. .
Malachite Green.	. .	Orange.	Orange.	Bleached.	Orange.	Decolorized.	. .
Helvetia Green.	. .	. .	Yellow.	Decolorized.	. .	Buff.	. .
Aldehyde Green.	. .	Yellow.	. .	Orange.	. .	Paler.	. .
Vat Indigo and Old Fustic.	. .	Paler.	Blue.	Paler.	Blue.	Green-blue.	Yellow.
Vat Indigo and Lead Chromate.	. .	Blue.	Yellow.	Yellow-green.	. .	Blue.	Yellow.
Indigo Carmine and Picric Acid.	. .	Blue, then much paler.	Blue.	As HCl.	Blue.	Decolorized.	Yellow.
Chrome Green.	. .	No action.	. .	No action.	.	No action.	. .
Azine Green.	L	Violet.	. .	Brown.	. .	Darker.	. .
Azo Green.	By	Brown.	Yellow.	Brown.	Yellow.	Yellower.	. .
Brilliant Green.	C	Yellow.	Yellow.	Red.	Red.	Decolorized.	. .
Diamond Green.	By	Bluer.	Yellow.	Bluer.	Blue.	. .	. .
Dioxin.	L	Dk. brown.	Brown.	Dk. green.	Black.	Dk. brown.	Red.
Alizarin Green SW.	B	Redder.	Pink.	Blue.	Blue.	Greener.	. .
Fast Green.	B	Amber.	. .	Yellow.	. .	Greener.	. .
Guinea Green.	A	Yellowish.	. .	Brown.	. .	Decolor.	. .
Gambin.	H	Olive.	Yellow.	Olive.	Brown.	No action.	. .
Indoine Blue 2 B.	B	Green.	Yellow.	Dark green.	Green.	. .	. .
Light Green SF.	B	Orange.	Yellow.	Orange.	Yellow.	Decolor.	. .
Light Green S.	B	Brown.	Brown.	Red-brown.	Yellow.	Decolor.	. .
Naphthol Green.	C	Yellow.	Yellow.	Olive.	Drab.	Brighter.	Olive.
Victoria Green.	. .	Orange.	. .	Yellow.	Yellow.	Decolor.	. .

IV. GREEN COLORS.

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
No action.	. .	Brown.	Red.	No action.	. . .
No action.	. .	Brown.	Paler.	No action.	Ash contains Fe.
Decolor.	. .	. .	Decolorized.	Green.	. . .
Decolor.	. .	. .	No change.	Green.	. . .
Decolor-ized.	. .	. .	Decolorized.	Blue-green.	Heated to 100°—violet (distinction from Malachite Green).
Decolor-ized.	. .	. .	Decolorized.	Green.	. . .
Buff.	.	. .	Decolorized.	Bluish-green.	. . .
Paler.	. .	Brown.	Decolorized.	Green.	. . .
Blue.	Greenish.	. .	Paler.	See Indigo.	Boiling solution $Al_2(SO_4)_3$—yellow with green fluor.
No action.	. .	. .	Blue, then de-colorized.	See Indigo.	Ash contains Pb and Cr.
Decolor-ized.	Yellow.	. .	Decolorized.	. .	Cold water extracts picric acid.
No action.	. .	. .	No action.	No action.	$CaOCl_2$—yellow sol.
. .	. .	Brown.	Brighter.	Green.	. . .
Decolor.	. .	Yellow.	Yellower.	Bluish-green.	. . .
Decolor-ized.	. .	Orange.	Yellower.	Green.	. . .
. .	. .	Red.	Brighter.	. .	Ash contains Cr.
Dk. brown.	Brown.	. .	.	Green-yellow.	Ash contains Fe.
Greener.	. .	Brown.	Gray.	No action.	Ash contains Cr.
. .	. .	Yellow.	Lighter.	Pale green.	. . .
Decolor.	. .	Orange.	. .	. .	. .
No action.	. .	Red.	No change.	Pale yellow.	Ash contains Fe.
Lighter.	. .	Yellowish.	. .	Blue.	. . .
Decolor.	. .	Yellow.	Brighter.	Pale green.	. . .
Decolor.	. .	Orange.	. .	. .	. . .
No action.	. .	Orange.	Decolorized.	Pale blue.	. . .
Decolor.	. .	Red	No change.	Green.	. . .

V. YELLOW COLORS.

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Picric Acid.	. .	Decolor.	Yellow.	Decolor.	. .	Orange.	Yellow.
Victoria Yellow.	. .	Decolorized.	. .	. .	. .	. .	.*.
Naphthol Yellow.	. .	Decolorized.	Colorless.	Decolorized.	. .	Orange.	Yellow.
Naphthol Yellow S.	. .	Decolorized.	Colorless.	Decolorized.	. .	Paler.	Yellow.
Aurantia.	. .	Paler.	. .	Drab.	. .	No action.	. .
Quinoline Yellow.	B	Yellow.	Colorless.	Yellow.	Colorless.	Decolorized.	. .
Chrysoidine Yellow.	BSS	Red.	. .	. .	Yellow.	Paler.	. .
Fast Yellow.	B	Red.	. .	Brown.	. .	No action.	. .
Orange II.	P	Violet.	Violet.	Violet.	Violet	Deep red.	. .
Orange III.	By	Red.	Pink.	Violet.	Violet.	Yellowish.	. .
Orange IV.	P	Violet.	Violet.	Violet.	Violet.	No action.	. .
Citronin.	. .	Violet.	Violet.	Violet.	Violet.	Green-yellow.	Colorless.
Croceïn Orange.	By	Brown.	Pink.	Darker.	Orange.	Brown.	. .
Chrysamine.	By	Brown.	Pink.	Magenta.	Violet.	Dark orange.	Colorless.
Hessian Yellow.	M	Black.	Violet.	Dark violet.	Violet.	Dark red.	Pink.
Brilliant Yellow.	M	Dark violet.	. .	Black.	Violet.	Red.	Pink.
Chrysophenine.	By	Black.	Colorless.	Brown.	. .	No change.	Yellowish.
Primuline Yellow.	BSS	No action.	. .	Paler.	. .	Brighter.	Colorless.
Toluylene Orange.	O	Violet.	Reddish.	Magenta.	Colorless.	Brighter.	. .
Toluylene Orange R.	O	Paler.	Yellow.	Yellowish.	Yellow.	Redder.	Colorless.
Primuline Orange.	BSS	Brown.	Brown.	Brown.	Dark red.	Dark brown.	. .
Oriol.	G	Red.	Red.	Red.	Red.	Redder.	Colorless.
Auramine.	B	Decolor.	Colorless.	Decolor.	Colorless.	Decolor.	Colorless.
Curcumin W.	A	Black.	. .	Black.	Violet.	Red.	Pink.
Phosphine.	. .	Decolorized.	Yellow.	. .	Green-yellow.	Paler.	. .

V. YELLOW COLORS.

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Paler.	Yellow.	. .	Decolorized.	Yellow.	KCN—red.
No change.	. .	. .	. .	. .	Warm water extracts the color.
Paler.	Yellow,	.	Decolorized.	Yellow.	KCN—red. Stains paper at 120°.
No change.	Yellow.	. .	Bleached.	No action.	. . .
No action.	. .	. .	Brown.	Yellow.	. . .
No action.	. .	Deep yellow.	No change.	No action.	. . .
Yellower.	. .	. .	Decolorized.	Yellow.	. . .
No action.	. .	Red.	Decolorized.	Pale yellow.	. . .
No action.	. .	. .	Decolorized.	No action.	. . .
No change.	Yellow.	. .	Decolorized.	Pale yellow.	. . .
No change.	Yellow.	. .	Decolorized.	Yellow.	. . .
No change.	Colorless.	Violet.	Decolorized.	Pale yellow.	. . .
No action.	. .	Black.	Decolorized on boiling.	Pale orange.	$CaOCl_2$—decolorized.
Bright orange.	Colorless.	Gray.	Decolorized.	No action.	. . .
Dark orange.	Orange.	Brown.	Decolorized.	No action.	. . .
Red.	Pink.	. .	Decolorized.	No action.	. . .
No action.	. .	Violet.	Decolorized.	No action.	. . .
No action.	. .	. .	Slight action.	No action.	. . .
No action.	. .	Gray.	Decolorized.	No action.	. . .
No action.	. .	Violet.	Decolorized.	No action.	. . .
No action.	. .	Brown.	Decolorized.	Pale orange.	. . .
Orange.	. .	Orange-red.	Decolorized.	No action.	Very fast to light.
Paler.	Colorless.	White.	Decolorized.	No action.	. . .
Red.	Pink.	. .	Decolorized.	No action.	. . .
Paler.	. .	. .	Decolorized.	Pale yellow.	. . .

V. YELLOW COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Tartrazin.	B	Orange.	Yellow.	Orange.	Yellow.	Orange.	Yellow.
Nitro Alizarin.	. .	Straw yellow.	Yellow.	Brownish.	Yellow.	Claret.	Colorless.
Galloflavine.	B	Darker.	Yellow.	Darker.	Yellow.	Darker.	Yellow.
Madder.	. .	No action.	.	Red.	Red.	Purple.	Purple.
Quercitron Bark.	. .	No change.	Yellow.	Yellow.	Yellow.	No change.	Yellow.
Flavin.	. .	Yellow.	Yellow.	Yellow.	Yellow.	Yellow.	Yellow.
Old Fustic.	. .	Orange.	Orange.	Brown.	Brown.	No change.	. .
Young Fustic.	. .	No change.	Yellow.	Brown.	Brown.	Brown.	. .
Weld.	. .	No change.	Yellow.	Bright yellow.	. .	No change.	Yellow.
Persian Berries.	. .	No change.	Yellow.	Brown.	Yellow.	No change.	Yellow.
Annatto.	. .	No change.	Red.	Blue.	Blue.	No action.	. .
Turmeric.	. .	Brown.	Colorless.	Brown.	Brown.	Brown.	Brown.
Iron Buff.	. .	Decolor.	. .	No action.	. .	No action.	. .
Chrome Yellow.	. .	Decolorized.	Yellow.	Duller.	. .	Redder.	Yellow.
Azo Flavin.	B	Violet.	Crimson.	Violet.	. .	Greener.	. .
Uranin G.	B	Brighter.	Yellow.	Greener.	Yellow.	Orange.	Yellow.
Alizarin Yellow A.	B	No change.	. .	Dull yellow.	Pale yellow.	Darker.	. .
Anthracene Yellow.	C	Dark purple.	. .	Maroon.	Maroon.	Darker.	. .
Diamond Yellow G.	By	Orange.	Yellow.	Red.	. .	Darker.	. .
Flavazol.	A	Crimson.	Yellow.	Scarlet.	Orange.	No change.	. .
Patent Fustin.	. .	Bright red.	Yellow.	Bright red.	Red.	Brown.	Brown.
Thioflavine T.	C	Decolorized.	. .	Brown.	. .	Decolorized.	. .
Milling Yellow O.	C	Crimson.	Crimson.	Crimson.	Red.	. .	. .
Yellow N.	P	Violet.	Violet.	Dull green.	Violet.	. .	. .
Tropæolin OO.	C	Violet.	Violet.	Violet.	Violet.	Brighter.	. .
Metanil Yellow.	O	Purple.	Purple.	Dark purple.	. .	Brighter.	. .
Orange G.	II	Scarlet.	Pink.	Crimson.	Red.	Terra-cotta.	. .

V. YELLOW COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Orange.	Yellow.	No action.	Decolorized.	No action.	. . .
No action.	. .	Yellow.	Deep yellow.	No action.	Ash contains Cr.
Darker.	Colorless.	. .	No action.	. .	Fe_2Cl_6—olive-green.
Brown.	. .	. .	No change.	No action.	Fe_2Cl_6—olive-brown.
No change.	Yellow.	Blue.	No change.	No action.	Fe_2Cl_6—olive.
No change.	Yellow.	Dark brown.	Brown-yellow.	No action.	Fe_2Cl_6—olive.
No change.	Yellow.	Pale yellow.	Orange.	No action.	Fe_2Cl_6—olive.
Brown.	. .	Dark brown.	No action.	No action.	Fe_2Cl_6—olive.
No action.	. .	No action.	No change.	No action.	Fe_2Cl_6—olive.
. .	Pale yellow.	Brown.	Brown.	No action.	Fe_2Cl_6—olive.
No action.	. .	. .	Decolorized.	Yellow.	$K_3Fe(CN)_6$—blue.
Brown.	Orange.	Yellow.	Brown.	Yellow.	Ash contains Al.
No action.	. .	. .	Decolorized.	No action.	H_2S—black.
No action.	. .	. .	Decolorized.	No action.	H_2S—black.
No change.	. .	Red.	Lighter.	No action.	. . .
Redder.	Yellow.	No change.	No change.	Yellow.	. . .
Darker.	. .	Greenish.	. .	. .	Ash contains Cr.
Darker.	. .	Orange.	. .	. .	Ash contains Cr.
Darker.	. .	Orange.	Brown.	. .	Ash contains Cr.
No change.	. .	Scarlet.	Scarlet.	. .	. . .
Brown.	Brown.	Red.	Terra-cotta.	. .	. . .
Lighter.	. .	. .	Brighter.	Greenish-yellow.	. . .
Brighter.	. .	Red.	Decolorized.	Pale yellow.	. . .
Brighter.	. .	Yellow.	. .	Pale yellow.	. . .
Brighter.	. .	Red.	Darker.	Amber.	. . .
No change.	. .	Red.	Brown.	Pale yellow.	. . .
No change.	. .	Yellow.	Decolorized.	. .	. . .

V. YELLOW COLORS.—*Concluded.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Orange GT.	By	Red.	Pink.	Crimson.	Crimson.	Darker.	. .
Orange R.	. .	Scarlet.	Pink.	Crimson.	Red.	Terra-cotta.	. .
Alizarin Orange W.	B	Lighter.	Yellow.	Darker.	Brown.	Redder.	. .
Alizarin Orange S.	By	Yellow.	Yellow.	Darker.	Brown.	Redder.	. .
Benzoflavine.	.	Orange.	. .	Lighter.	. .	Lighter.	. .
Benzo Orange R.	. .	Blue.	Colorless.	Blue.	Blue.	Crimson.	Colorless.
Cloth Orange.	.	Violet.	. .	Violet.	Violet.	Darker.	. .
Chrysamin R.	. .	Violet.	. .	Violet.	. .	Pink.	. .
Carbazol Yellow.	. .	Slate.	Colorless.	Blue.	Blue.	Orange.	Pink.
Clayton Yellow.	Cl	Orange.	Colorless.	Brownish.	. .	Scarlet.	Colorless.
Cotton Yellow G.	. .	Crimson.	Colorless.	Red.	Red.	Orange.	Orange.
Curcumin S.	.	Duller.	. .	Brown.	. .	Redder.	. .
Cresotin Yellow G.	. .	Violet.	Colorless.	Violet.	Violet.	Red.	Pink.
Congo Orange.	. .	Violet.	. .	Blue.	Blue.	No change.	.
Thioflavine T.	. .	Decolor-ized.	.	Olive-green.	. .	Darker.	. .
Thioflavine S.	. .	Lighter.	Yellow.	Red.	Colorless.	No change.	. .
Thiazol Yellow.	. .	Orange.	. .	Brown.	Colorless.	Scarlet.	Colorless.
Mimosa.	. .	Orange.	. .	Dark yellow.	. .	Red.	. .
Diamine Yellow N.	. .	Violet,	. .	Violet.	Violet.	Orange.	Pink.
Mikado Orange 4 R.	. .	Olive.	. .	Blue.	. .	No change.	. .
Mikado Orange R.	. .	Olive.	. .	Gray.	. .	No change.	.
Nitrazine Yellow.	O	. .	Yellow.	. .	Yellow.	. .	Yellow.
Poppy 2 G.	A	Red.	Red.	Deep red.	Scarlet.	. .	Red.
Acridine Orange.	L	Red.	Red.	Decolor-ized.	Colorless.	Bright yellow.	Yellow.
Oxyphenine.	Cl	No change.	Yellow.	Red.	Brown.	No action.	. . .
Aurotine.	Cl	Decolor.	Colorless.	Brown.	Colorless.	Redder.	Yellow.

V. YELLOW COLORS.—*Concluded.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
. .	. .	. .	.	. .	. . .
. .	. .	Yellow.	. .	. .	. . .
Redder.	. .	Yellow.	No change.	No action.	Ash contains Cr.
Redder.	. .	Yellow.	. .	No action.	Ash contains Cr.
Lighter.	. .	. .	Decolorized.	Green-yellow.	On cotton.
Scarlet.	Colorless.	Brown.	Decolorized.	Pale orange.	On cotton.
Darker.	Pink.	Red.	. .	Yellow.	. . .
Orange.	. .	. .	Decolorized.	Yellow.	On cotton.
Redder.	Colorless.	Crimson.	Decolorized.	No action.	On cotton.
Orange.	Colorless.	Decolor.	Orange.	Yellow.	On cotton.
No change.	. .	Crimson.	Decolorized.	Yellow.	On cotton.
Redder.	. .	. .	Decolorized.	No action.	On cotton.
Orange.	Colorless.	Violet.	Decolorized.	Yellow.	On cotton.
No change.	. .	Crimson.	Decolorized.	Orange.	On cotton.
Lighter.	. .	. .	Decolorized.	Yellow.	On cotton.
No change.	. .	Brown.	Orange.	Yellow.	On cotton.
Orange.	Colorless.	Lighter.	Orange.	No action.	On cotton.
Orange.	. .	. .	Decolorized.	Yellow.	On cotton.
Orange.	Colorless.	Violet.	Decolorized.	Yellow.	On cotton.
No change.	. .	Slate.	Decolorized.	No action.	On cotton.
No change.	. .	Olive.	Decolorized.	No action.	On cotton.
. .	Yellow.	. .	Decolorized.	No action.	. . .
. .	Red.	Red.	Decolorized.	. .	. . .
. .	Yellow.	Brighter.	Purple.	Yellow.	. . .
No action.	. .	No change.	Decolorized.	No action.	On cotton.
. .	Yellow.	Lighter.	Decolorized.	No action.	. . .

VI. BROWN COLORS.

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Catechu Brown.	. .	No change.	Orange.	No change.	. .	No change.	. .
Bismark Brown.	. .	Reddish.	Red.	Reddish.	Red.	Yellower.	Colorless.
Phenyl Brown.	. .	Paler.	Brown.	. .	. .	Paler.	Purple.
Benzo Brown.	By	Darker.	Purple.	Black.	Brown.	No action.	. .
Fast Brown RG.	A	Violet.	Violet.	Violet.	Violet.	Crimson.	Red.
Naphthyla- mine Brown.	. .	Yellow.	Orange.	. .	. .	. .	. .
Alizarin Brown.	. .	Orange.	. .	Orange.	. .	Bluer.	Bluish.
Anthracene Brown.	B	Yellower.	Yellow.	Redder.	Brown.	Black.	Gray.
Peachwood.	. .	Orange.	Orange.	Orange.	Yellow.	Purple.	Red.
Camwood.	. .	Red.	Orange.	Red.	Orange.	Purple.	Purple.
Manganese Brown.	. .	Decolor- ized.	. .	No action.	. .	No action.	. .
Fast Brown.	By	Maroon.	Pink.	Violet.	Violet.	Scarlet.	. .
Fast Brown.	M	Crimson.	Pink.	Bluer.	Blue.	Darker.	. .
Fast Brown 3 B.	A	Violet.	Violet.	Blue.	Purple.	Crimson.	. .
Acid Brown R.	A	Violet.	Violet.	Violet.	Violet.	Scarlet.	. .
Acid Brown G.	A	Darker.	Yellow.	Purple.	Purple.	Darker.	. .
Benzo Brown B.	. .	Darker.	Brown.	Purple.	. .	No change.	. .
Benzo Brown G.	. .	Dark brown.	Light brown.	Darker.	Gray.	No change.	. .
Cloth Brown.	By	Violet.	. .	Violet.	Violet.	Darker.	. .
Congo Brown R.	. .	Violet.	. .	Violet.	. .	Crimson.	. .
Cotton Brown R.	. .	No change.	Orange.	Crimson.	Crimson.	No change.	. .
Congo Brown V.	. .	Violet.	Colorless.	Violet.	Violet.	Crimson.	Pink.
Congo Brown NBR.	. .	Violet.	Colorless.	Blue.	Blue.	Redder.	Colorless.
Cotton Brown A.	. .	Darker.	Colorless.	Dark green.	. .	No change.	. .
Cotton Brown N.	. .	Darker.	Brown.	Black.	Gray.	No change.	. .

VI. BROWN COLORS.

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO- CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
No change.	. .	. .	Paler.	No action.	Ash contains Cr.
No change.	Brown.	. .	Decolorized.	Pink.	Boiling water extracts color.
Paler.	Red brown.	. .	Pink.	Dark brown.	. . .
No action.	. .	. .	Yellower.	Pale brown.	. . .
Crimson.	Red.	Black.	Decolorized.	No action.	. . .
Yellow.	. .	. .	Purple.	Pink.	. . .
No change.	. .	. .	Orange.	No action.	. . .
Gray.	Colorless.	Black.	Yellow.	Pale brown.	. . .
Purple.	Colorless.	. .	Red.	. .	. . .
Purple.	Colorless.	. .	Red.	. .	On wool only.
No action.	. .	. .	Decolorized.	No action.	Ash contains Mn.
Yellower.	Brown.	Yellow.	Lighter.	. .	. . .
Darker.	. .	Yellow.	. .	Red.	. . .
Crimson.	Pink.	Orange.	Bluer.	. .	. . .
Scarlet.	Pink.	Yellow.	Decolorized.	Pale yellow.	. . .
Brighter.	Brown.	Yellow.	No change.	Brown.	. . .
No change.	Brown.	Darker.	Lighter.	Pale brown.	On cotton.
No change.	Orange.	Darker.	Lighter.	Pale brown.	On cotton.
Darker.	. .	Red.	No change.	. .	. .
Lighter.	. .	. .	Decolorized.	Pale brown.	On cotton.
No change.	. .	Brown.	Lighter.	Orange.	On cotton.
Scarlet.	Pink.	Red.	Decolorized.	Brown.	On cotton.
Redder.	Pink.	No change.	Lighter.	Brown.	On cotton.
No change.	. .	No change.	Decolorized.	Brown.	On cotton.
No change.	Orange.	Darker.	Lighter.	Brown.	On cotton.

VI. BROWN COLORS.—*Concluded.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Congo Brown G.	. .	Violet.	Colorless.	Violet.	Violet.	Crimson.	Crimson.
Dioxin.	L	Darker.	Brown.	Green.	Green.	Dark green.	. .
Diamine Brown V.	. .	No change.	. .	Purple.	Purple.	No change.	Pink.
Gambin.	H	No change.	. .	Brown.	Brown.	Yellower.	Yellow.
Hessian Brown 2 B.	. .	Drab.	. .	Violet.	. .	No change.	. .
Mikado Brown G.	. .	Buff.	Colorless.	Violet.	Violet.	No change.	. .
Toluylene Brown.	. .	Darker.	Pink.	Violet.	Violet.	No change.	. .

VII. BLACK COLORS.

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Tannin Black.	. .	Straw.	. .	Straw.	. .	Gray.	. .
Naphthol Black.	M	. .	Reddish.	. .	Olive green.	. .	Reddish.
Brilliant Black.	B	. .	Violet.	. .	. .	Greener.	Violet.
Resorcin Black.	DH	Gray.	Brown.	Brown.	Brown.	. .	Green.
Wool Black.	A	Black.	Blue.	Black.	Blue.	No action.	. .
Aniline Black.	. .	No action.	. .	No action.	. .	No action.	. .
Alizarin Black.	. .	Orange.	. .	Orange.	. .	No action.	. .
Alizarin Black.	B	Black.	Violet.	Black.	Blue.	Black.	Blue.
Woaded Black.	. .	Blue.	Violet.	Blue.	Violet.	Blue.	Violet.
Logwood Black.	. .	Brown.	Red.	Brown.	Red.	. .	Purple.
Naphthol Black B.	C	No change.	. .	Green.	Blue.	No change.	. .
Naphthol Black 3 B.	C	. .	. .	Green.	Blue.	. .	. .
Naphthol Black 6 B.	C	Redder.	Colorless.	Greener.	Greenish.	. .	. .
Naphthyl-amine Black D.	C	No change.	Green.	. .	Violet.	Bluer.	Blue.

VI. BROWN COLORS.—*Concluded.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
Redder.	. .	Violet.	Decolorized.	Yellow.	On cotton.
Dark green.	Red.	. .	. .	. .	Ash contains Cr.
No change.	. .	Violet.	Decolorized.	Pale red.	On cotton.
No change.	. .	Yellow.	Redder.	No action.	Ash contains Cr.
No change.	. .	. .	Decolorized.	Pale brown.	On cotton.
No change.	. .	Olive.	Decolorized.	No action.	On cotton.
No change.	. .	Brown.	Decolorized.	No action.	On cotton.

VII. BLACK COLORS.

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
No action.	. .	. .	Decolorized.	No action.	Ash contains Fe.
No action.	. .	Brown.	Decolorized.	No action.	. . .
. .	Violet	Brown.	Decolorized.	No action.	. . .
No action.	. .	Yellow.	Brown.	No action.	Ash contains Fe.
No action.	. .	Red-brown.	Decolorized.	No action.	. . .
No action.	. .	. .	Green-gray.	Brown-red.	$CaOCl_2$—brown-red.
No action.	. .	. .	Orange.	No action.	Ash contains Fe.
No action.	. .	Olive-green.	Brownish.	No action.	. . .
Blue.	Violet.	. .	Green-blue.	Indigo removed.	. . .
. .	Purple.	. .	Violet.	No action.	Ash contains Fe or Cr.
Violet.	Violet.	Red.	Crimson.	. .	. . .
Violet.	Violet.	Red.	Crimson.	. .	. . .
. .	Blue.	Red.	Purple.	. .	. . .
. .	Violet.	Brown.	No change.	Violet.	. . .

VII. BLACK COLORS.—*Continued.*

DYESTUFF.	FIRM.	HYDROCHLORIC ACID.		SULPHURIC ACID.		CAUSTIC SODA.	
		Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Anthracite Black D.	C	Violet.	. .	Greener.	Gray.	No change.	Pink.
Victoria Black 5 G.	By	Greener.	Colorless.	. .	Green.	Dark green.	Green.
Victoria Black Blue.	By	. .	. .	. .	Green.	Greener.	Violet.
Jet Black R.	By	. .	Green.	Blue.	Blue.	Dark green.	. .
Wool Gray.	M	Lighter.	Maroon.	Maroon.	Gray.	Brown.	. .
Diamond Black.	By	Green.	. .	Greener.	Green.	Darker.	Gray.
Nigrosine, soluble.	B	Slate.	. .	Slate.	Gray.	Brown.	. .
Nigrosine.	A	Darker.	Purple.	Violet.	Blue.	Maroon. ·	. .
Benzo Black S.	. .	Violet.	. .	Violet.	Violet.	Violet.	Red.
Benzo Blue Black R.	. .	. .	. .	Blue.	Blue.	Violet.	. .
Violet Black.	. .	Bluer.	. .	Blue.	Blue.	. .	Pink.
Benzo Gray S.	. .	Bluer.	. .	Violet.	Blue.	Violet.	. .
Diamine Black BO.	C	Redder.	. .	Blue.	Blue.	Redder.	Pink.
Same developed with phenylene-diamine.	C	. .	. .	Blue.	. .	. .	. .
Diamine Black RO.	C	Redder.	. .	Blue.	Blue.	Violet.	Pink.
Same developed with phenylene-diamine.	C	. .	. .	Darker.	. .	. .	. .
Diazo Black R (with β-naph-thol).	By	. .	. .	Navy blue.	Navy blue.	. .	Rose.
Diazo Brilliant Black B.	By	Greenish blue.	. .	Indigo blue.	Indigo blue.	. .	. .
Diamine Deep Black OO.	C	Dark violet.	Dark violet.	Dark blue.	Blue.	Red.	Red.

VII. BLACK COLORS.—*Continued.*

AMMONIA.		SPOT WITH NITRIC ACID.	STANNOUS CHLORIDE AND HYDRO-CHLORIC ACID.	ALCOHOL.	REMARKS.
Fibre.	Solution.				
. .	. .	Yellow,	Violet.	Violet.	. . .
. .	Violet.	Red.	Decolorized.	. .	. . .
. .	Violet.	Orange.	. .	. .	. . .
. .	. .	Yellow.	Decolorized.	Green.	. . .
Brown.	. .	Yellow.	Violet.	Violet.	. . .
. .	Gray.	Red.	. .	Violet.	Ash contains Cr.
Brown.	Gray.	. .	. .	. .	. . .
Maroon.	. .	. .	. .	. .	. . .
Violet.	Pink.	Scarlet.	Decolorized.	Violet.	On cotton.
Violet.	Pink.	Brown.	Decolorized.	Violet.	On cotton.
. .	Violet.	Orange.	Decolorized.	Crimson.	On cotton.
Redder.	. .	Scarlet.	Decolorized.	Violet.	On cotton.
. .	. .	Violet.	Decolorized.	Violet.	On cotton.
. .	. .	. .	Decolorized.	Violet.	On cotton.
. .	. .	Violet.	Decolorized.	Violet.	On cotton.
. .	. .	. .	Decolorized.	Violet.	On cotton.
. .	Rose.	Brown.	Decolorized.	. .	. . .
. .	. .	Violet.	Decolorized.	. .	. . .
. .	Violet.	Brown.	Decolorized.	. .	. . .

WRITING INKS.

Writing inks are either colored liquids, or liquids containing a finely-divided precipitate in suspension.

Ordinary writing ink was formerly always made from a decoction of galls, to which green vitriol was added. Of late, the composition of writing inks has become far less constant, aniline and other dyes being frequently employed, and other metallic salts substituted for the ferrous sulphate formerly invariably used.

The table following shows the general composition of black writing inks, and sufficiently indicates the nature of the substances to be sought for by the analyst:—

	Superior Ink.	Inferior Ink.	Ink containing Vinegar.	Logwood Ink.	Copying Ink.	Copper Ink.	Runge's Chrome Ink.	Copying Ink.	Ink Powder.	Stephen's Blue-Black Ink.
Galls, ...	225	62	174	50	60	42	. .	. .	12	15
Logwood, . . .	. .	. .	. .	100	21	20	140	4	. .	. .
Potassium chromate, . . .	. .	. .	. .	. .	. .	. .	1	. .	. .	. .
Ferrous sulphate,	75	31	87	16	20	21	. .	3	5	5
Cupric sulphate,	. .	. .	. .	. .	. .	5	. .	. .	. .	4 iron filings.
Alum, ...	. .	. .	. .	. .	. .	. .	. .	2	. .	. .
Gum, ...	25	31	43	47	20	16	. .	3	2	. .
Sugar, ...	. .	. .	. .	28	1000(?)	. .	. .	5	1	. .
Vinegar, ...	. .	. .	135	. .	. .	. .	. .	60	. .	. .
Water, . . . , . .	1000	1000	1000	. .	1000	1000	1000	70	. .	200 ½ indigo in 3 of sulphuric acid.

The best black ink is a tanno-gallate of iron, obtained by adding an infusion of nut-galls to a solution of ferrous sulphate (copperas). The galls contain gallic and gallotannic acids, both of which are serviceable. On coming in contact with ferrous salts in concentrated solutions, these produce white precipitates which turn black on exposure to air. With ferric salts, blue-black precipitates are at once produced. A small quantity of gum is added to retain the precipitate in suspension. To ink intended for copying by pressure a small addition of sugar or glycerin is also made.

Sumac is sometimes used instead of galls, and some of the nut-gall inks contain a little acetic acid, added as vinegar.

Some of the gallic inks receive an addition of indigo-carmine or sulphindigotic acid. Aniline dyes are frequently used as a whole or part of the coloring matter of both black and colored inks.

According to R. Böttger an excellent black ink may be prepared by dissolving in water 1 part of pyrogallol, 3 of ammonium vanadate, and 3 of finely-powdered gum-arabic. Another highly recommended ink is made with nigrosine (an aniline black), potassium bichromate, and gelatin.

Logwood is a frequent constituent of ink. It gives the original ink a darker hue, and itself contains tannin, besides the coloring matter h æ m a t o x y l i n. Logwood and alum form a frequent basis of purple inks.

A very cheap and perfect ink is obtained by dissolving 24 parts of extract of logwood in 1,000 of water, and adding 2 parts of neutral potassium chromate. This ink is a deep black liquid, which, unlike that made with gallic acid and iron, contains no deposit.

Sulphate of copper is sometimes added to ink, with questionable advantage.

Indelible ink usually owes its permanency to an admixture of finely-divided carbon, to which indigo is sometimes added. It is kept in suspension by gluten, an alkaline solution of shellac, or other similar means.

In analyzing ink, the *total solid residue* should be determined by evaporating 50 c.c. to dryness on the water-bath. The residue thus obtained is first weighed and next ignited, the odor produced on heating being carefully noted ; sugar or shellac may thus be detected. The weight of the ignited residue is then taken, after which it is mixed with magnesia and caustic soda, and ignited in platinum. The mass is extracted with hot water, the solution filtered, and the filtrate acidulated with acetic acid. In presence of a chromate, the liquid will have a yellow color, and will give a chrome-yellow precipitate on adding acetate of lead. The precipitated $PbCrO_4$ may be collected and weighed, or the chromate formed determined volumetrically by a ferrous salt. The residue left on treating the fused mass with water should be boiled with hydrochloric acid, the liquid filtered and examined for iron, copper, aluminium, &c., in the usual way. By precipitating the solution with a large excess of ammonia, the iron and aluminium may be roughly separated from the copper, which remains in solution and communicates a blue color to the liquid.

For the detection of *organic coloring matters*, a portion of the ink should be strongly acidulated with hydrochloric acid. A blue color, unaffected by the acid, but destroyed on adding bromine

water or bleaching powder, shows the presence of indigo. If Prussian blue be present, the ink will probably turn brown on addition of soda, and the filtered liquid will give a deep blue precipitate with ferric chloride, after being acidified with hydrochloric acid. A black color, not destroyed by acids or alkalies, nor bleached by chlorine or bromine, is pretty certain to be due to finely-divided carbon. An ink prepared with ammonium vanadate and galls is turned blue by acids, but is unaffected by alkalies. Its color is altered but not bleached by chlorine. Aniline-black is not affected by alkalies, but is turned dark green by acids; bleaching powder renders it garnet-red. Logwood inks are turned red or yellow by hydrochloric acid, while those containing galls only are almost wholly decolorized by the same reagent.

Some inks have a great tendency to become mildewed; this may be prevented by a small addition of carbolic or salicylic acid. Essential oils are sometimes used for the same purpose.

G. W i s l a r (*Papier Zeit.* xx. 3059) recommends the comparison of a commercial sample of ink with a standard ink prepared by dissolving 23.4 grammes tannin and 7.7 grammes of crystallized gallic acid in water at 50° C., adding 10 grammes of gum, 2.5 grammes hydrochloric acid, 30 grammes of ferrous sulphate, and 1 gramme of phenol. The solution is made up to 1 litre and allowed to stand four days, when the clear solution is poured off. To this normal ink coloring matter is added to get the required shade. The ink to be tested, having stood for three days, is uncorked, and 50 c.c. is taken out of the centre of the liquid and filtered through a small, fine filter paper; 25 c.c. of the filtrate are placed in a cylindrical vessel, the neck is closed loosely with filter paper, and the liquid is allowed to stand for some time in diffused light and in contact with air free from ammonia and acid; if after 14 days there is a deposit on the walls of the vessel, the ink is unsatisfactory. In order to test the darkening qualities of the ink, a sheet of the best writing paper is stretched on a frame and placed at an angle of 45°, then a little of the unfiltered ink is allowed to run down the surface from a glass tube and form a streak on the paper. Another streak of the normal ink is formed in the same way by the side of the first, and both are allowed to dry; then if they compare favorably, both inks are diluted with an equal volume of water, and fresh streaks are made and compared. Further, the paper may be cut into strips across the streaks and treated with water, 85 per cent. alcohol, and 50 per cent. alcohol for two days;

after drying they are again compared. To test the fluidity, the ink is allowed to flow from an oval spreader and the width of the streak measured. The tendency to blot may be observed in the first test. The stickiness is tested by putting bits of paper on the dried ink, or by hand.

COLORED INKS do not usually contain tannic acid; in many instances they are nothing but solutions of coal-tar dyes. The following examples will suffice to give a general idea of their composition:—

Red.—Brazil wood, with stannous chloride or cream of tartar and alum; cochineal or carmine dissolved in ammonia or sodium silicate; aniline red.

Blue.—Prussian blue dissolves in oxalic acid; aniline blue.

Violet.—Aniline violet.

Green.—Acetate of copper and cream of tartar; chrome alum; iodine green.

MARKING INKS are all closely analogous in composition, and their assay requires no special description. They usually consist of nitrate of silver colored with sap-green, ivory-black, indigo, &c.; or ammonio-nitrate of silver mixed with sodium carbonate, sometimes with sulphate of copper added. In Redwood's ink, tartrate of silver is substituted for the nitrate. Reade's ink is ammonio-tartrate of silver.

PRINTING INK is made by suspending lampblack in linseed oil, with more or less rosin oil, rosin, turpentine, &c.

INVISIBLE INKS are such that give visible characters only after a chemical treatment of the writing. A solution of lead acetate may be used for this purpose, when the writing will become visible on exposure to vapors of hydrogen sulphide. Potassium ferrocyanide solution will give a writing which can be developed by moistening with a dilute solution of an iron salt. A writing which will fade away can be made by using an ink prepared from rice starch, water, and a few drops of tincture of iodine. The writing may be restored by exposing to the vapor of iodine.

CHEMICAL EXAMINATION OF INK MARKS.

In chemico-legal cases it is sometimes of importance to ascertain the nature of the ink used, to compare it with specimens of writing of known history, and to ascertain the relative ages of the writings. A minute inspection should first be made with a magnifying power of about 10 diameters, and any peculiarities of color, lustre, shade, &c., duly noted, and where lines cross each other

which lie uppermost. The examination is often facilitated by moistening the paper with benzene or petroleum spirit, whereby it is rendered semi-transparent. The use of alcohol or water is inadmissible.

Valuable information is often obtainable by treating writing or other ink-marks with reagents. Some inks are affected much more rapidly than others, though the rate of change depends greatly on the age of the writing. Normal oxalic acid (63 grammes per litre), or hydrochloric acid of corresponding strength, should be applied to a part of the ink marked with a feather or camel-hair brush (or the writing may be traced over with a quill pen), and the action observed by means of a lens, the reagent being allowed to dry on the paper.[1] Recent writing (one or two days old) in gallic inks is changed by one application of oxalic acid to a light gray, or by hydrochloric acid to yellow. Older stains resist longer, in proportion to their age, and a deeper color remains. Logwood ink marks are mostly reddened by oxalic acid, and alizarin marks become bluish, but aniline inks are unaffected. With hydrochloric acid, logwood ink marks turn reddish or reddish-gray, alizarin marks greenish, and aniline ink marks reddish or brownish-gray. The treatment with acid should be followed by exposure to ammonia vapors, or blotting paper wet with ammonia may be applied. Thus treated, marks in logwood ink turn dark violet or violet-black. The age of ink marks very greatly affects the rate of their fading when treated with dilute ammonia, the old marks being more refractory. The behavior of ink marks when treated with solution of bleaching powder is often characteristic, the older writings resisting longer; but unless the reagent be extremely dilute, writings of all ages are removed almost simultaneously (R. Irvine, *Jour. Soc. Chem. Ind.*, vi. 807). Hydrogen peroxide acts more slowly than bleaching solution, but gives more definite results. After bleaching the mark by either reagent, the iron of the ink remains mordanted on the paper, and the mark may be restored by treatment with a dilute solution of galls, tannic acid, or acidulated potassium ferrocyanide. The same reagents may be used for restoring writing which has been faded from age alone.

---

[1] The author succeeded by this treatment in detecting an alteration in a receipt on account in which a figure 1 had been altered to 4. The added mark, as also a forged signature across the stamp necessitated by the change, faded out first under treatment with dilute hydrochloric acid.

When ink marks have been erased or discharged by chemical means, traces of the treatment are often recognizable. After effecting the erasure, the spot is often rubbed over with powdered alum or gum sandarac, or coated with gelatin or size. The bleaching agents most likely to have been used are oxalic, citric, or hydrochloric acid, bleaching powder solution, or acid sulphite of sodium. Moistened litmus paper will indicate the presence of a free acid, and in some cases treatment with ammonia fumes will restore the color. The presence of calcium, chlorides, or sulphates in the water in which the paper is soaked will afford some indication of bleaching powder or a sulphite having been used. Potassium ferrocyanide will detect any iron remaining in the paper. Exposure to iodine vapor often affords evidence of chemical treatment, and other methods of examination readily suggest themselves.

The application of reagents to writing in black ink has been recommended by W. T h o m s o n for the identification of handwriting (*Chem. News*, xlii. 32).

R o b e r t s o n and H o f f m a n n (*Pharm. Centr.*, xxxiii. 225) propose a treatment of written characters with the following reagents in order to detect forgeries and alterations:

(1.) 3 per cent. solution of oxalic acid in water.

(2.) 10 per cent. solution of citric acid in water.

(3.) 2 per cent. solution of chloride of lime in water.

(4.) Solution of 1 part stannous chloride in 1 part of hydrochloric acid and 10 parts of water.

(5.) 15 per cent. sulphuric acid solution.

(6.) 10 per cent. hydrochloric acid solution.

(7.) 20 per cent. nitric acid solution.

(8.) Saturated solution of sulphur dioxide in water.

(9.) 4 per cent. solution of gold chloride in water.

(10.) Solution of 1 part potassium ferrocyanide in 1 part of hydrochloric acid and 10 parts water.

(11.) Solution of 1 part sodium thiosulphate in 1 part ammonia and 10 parts water.

(12.) 4 per cent. solution of sodium hydroxide.

These reagents should be applied by means of a quill pen drawn over the characters. Their action on a number of different inks is given in the following table. The reactions should be observed under a power of 100 diameters.

REAGENTS.	IRON GALLOTANNIC INK.	LOGWOOD.		NIGROSIN.	VANADIUM INK.	RESORCIN INK.
		With Potassium Chromate.	With Copper Sulphate.			
Oxalic acid.	Disappears.	Violet.	Orange-yellow.	Unchanged.	Fades, and runs a little.	Bright red.
Citric acid.	Fades.	Violet.	Orange-yellow.	Runs, with dark blue color.	Fades and runs.	Disappears.
Hydrochloric acid.	Disappears, but leaves behind a yellow coloration.	Purplish-red.	Blood-red.	Slightly altered.	Fades slightly and runs a little.	Bright pink.
Sulphuric acid.	Disappears.	Red.	Purplish-red.	Unchanged.	Fades a little.	Bright red.
Nitric acid.	Disappears.	Red.	Purplish-red.	Runs a little.	Fades a little.	Bright pink.
Stannous chloride.	Disappears.	Red.	Magenta-red.	Unchanged.	Fades a little.	Disappears.
Sulphurous acid.	Fades.	Grayish-violet.	Red.	Unchanged.	Fades a little and runs.	Fades.
Gold chloride.	Fades slightly.	Reddish-brown.	Brown.	Unchanged.	Unchanged.	Runs, with brown color.
Sodium thiosulphate and ammonia.	Dark red.	Unchanged.	Dark blue.	Dark violet, runs.	Runs very much.	Brown.
Potassium ferrocyanide and hydrochloric acid.	Blue.	Red.	Brick-red.	Unchanged.	Unchanged.	Pink.
Sodium hydroxide.	Dark red.	Brown.	Dark red, runs.	Dark violet, runs.	Dirty brown, runs.	Unchanged.
Chloride of lime.	Disappears.	Disappears.	Disappears, but leaves a yellow coloration.	Brown.	Unchanged.	Brown.

When characters have been removed unchemically, proof may be obtained by means of a photograph taken by transmitted light, or by exposing the paper to iodine vapor. The latter process is especially useful in cases where, for the removal of the writing, the paper has been moistened; these places become blue, the other brown. When the removal has been effected by chemical means, in most cases by oxalic acid, chloride of lime and sulphur dioxide, the suspected places are treated with a solution of sulphur dioxide in water, then with 3 per cent. solution of hydrogen peroxide, and finally with dilute ammonia. After the evaporation of the excess of ammonia, good results may be obtained with tannin, which darkens the characters.

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